ENHANCED BIOGAS PRODUCTION EFFICIENCY FROM LONGAN LEAVES (*Dimocarpus longan*) WITH CO-DIGESTION OF ANIMAL MANURE BY SOLAR HEATING

WEERAPONG PANTUMIT

MASTER OF ENGINEERING IN RENEWABLE ENERGY ENGINEERING
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A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENGINEERING
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ชื่อเรื่อง	การเพิ่มประสิทธิภาพการผลิตก๊าซชีวภาพจากใบลำไยที่หมักร่วมกับมูลสัตว์โดยความร้อนแสงอาทิตย์
ชื่อผู้เขียน	นายวีระพงศ์ พันธุมิตร
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บทคัดย่อ

ประเทศไทยเป็นประเทศเกษตรกรรมที่เป็นผู้ผลิตและส่งออกลำไย อุตสาหกรรมการค้าลำไยได้เติบโตอย่างรวดเร็ว ซึ่งผลไม้นี้ได้รับการปลูกกันอย่างแพร่หลายในประเทศไทย โดยเฉพาะอย่างยิ่งในเขตภาคเหนือ ในขณะเดียวกันการผลิตลำไยก่อให้เกิดวัสดุเหลือทิ้งจำนวนมาก เช่น ใบและกิ่งก้านหลังจากการตัดแต่ง ดังนั้นในการศึกษาครั้งนี้จึงใช้วัสดุเหลือทิ้งทางการเกษตร (ใบลำไย) และมูลสุกรสำหรับการผลิตก๊าซชีวภาพ โดยงานวิจัยนี้ได้แบ่งออกเป็น 3 ส่วน ในส่วนแรก เป็นการประเมินผลผลิตก๊าซชีวภาพจากใบลำไย (*Dimocarpus longan*) ด้วยการวิเคราะห์องค์ประกอบทางเคมีของใบลำไย พบว่า ปริมาณคาร์บอน ไฮโดรเจน ออกซิเจน ไนโตรเจน และ ซัลเฟอร์ มีค่าเท่ากับ 47.33%, 5.69%, 40%, 5.67% และ 0.23% ตามลำดับ นอกจากนี้ใบลำไยยังมีความชื้น 9.61% และขี้เถ้า 7.46% เมื่อวิเคราะห์โดยใช้น้ำหนักแห้ง ปริมาณของแข็งทั้งหมด (TS) ปริมาณของแข็งระเหยง่าย (VS) และความเป็น กรด-ด่าง (pH) ของใบลำไย มีค่าเท่ากับ 892,473 มิลลิกรัม/กิโลกรัม 833,384 มิลลิกรัม/กิโลกรัม และ 4.68 ตามลำดับ องค์ประกอบของก๊าซชีวภาพที่ประเมินได้ ประกอบด้วยมีเทน 43.66% คาร์บอนออกไซด์ 47.03% และแอมโมเนีย 9.31% ผลผลิตที่ได้จากการประมาณทางทฤษฎี ทำให้ได้ก๊าซชีวภาพทั้งหมด 0.9068 ลูกบาศก์เมตร/กิโลกรัม และมีปริมาณก๊าซมีเทนทั้งหมดเท่ากับ 0.2081 ลูกบาศก์เมตร ในการทดลองส่วนที่สอง เป็นการประเมินประสิทธิภาพของการปรับสภาพใบลำไยสำหรับการผลิตก๊าซชีวภาพโดยหมักร่วมกับมูลสุกร การปรับสภาพใบลำไยแบ่งออกเป็นการใช้ความร้อนด้วยวิธีการต้มที่ 100 องศาเซลเซียส เป็นเวลา 2 ชั่วโมง การปรับสภาพด้วยสารเคมีโดยใช้โซเดียมไฮดรอกไซด์ เป็นเวลา 72 ชั่วโมง และการปรับสภาพด้วยสารเคมีโซเดียมไฮดรอกไซด์ที่อุณหภูมิจากความร้อนแสงอาทิตย์ 60 องศาเซลเซียส เป็นเวลา 72 ชั่วโมง อัตราส่วนในการหมักใบลำไยและมูลสุกรเท่ากับ 10%TS (โดยใช้อัตราส่วนที่ดีที่สุดที่ 5:5 จากการวิเคราะห์ด้วยวิธีพื้นผิวตอบสนอง) พบว่า ผลผลิตก๊าซชีวภาพสะสมจากการปรับสภาพใบลำไยก่อนการหมัก ด้วยการต้มที่ 100 องศาเซลเซียส เป็นเวลา 2 ชั่วโมง ปรับสภาพด้วยโซเดียมไฮดรอกไซด์ เป็นเวลา 72 ชั่วโมง และการปรับสภาพด้วยโซเดียมไฮดรอกไซด์ที่อุณหภูมิ 60 องศาเซลเซียส เป็นเวลา 72 ชั่วโมง มีค่าเท่ากับ

8,903, 12,616 และ 13,221 มิลลิลิตร ตามลำดับ และความเข้มข้นของก๊าซมีเทนสูงสุด มีค่าเท่ากับ 54.5, 60.1 และ 60.7% ตามลำดับ ในการทดลองส่วนที่สาม เป็นการทดลองโดยขยายขนาดให้ใหญ่ขึ้น โดยเลือกอัตราส่วนที่ดีที่สุดและการปรับสภาพทางเคมีมาใช้ในการทดลองครั้งนี้ ซึ่งการทดลองนี้แสดงให้เห็นถึงการเพิ่มประสิทธิภาพในการผลิตก๊าซชีวภาพ ด้วยการออกแบบการใช้ความร้อนจากแสงอาทิตย์มาเพิ่มอุณหภูมิภายในถังหมักก๊าซชีวภาพขนาด 200 ลิตร ที่มีปริมาตรการทำงาน 170 ลิตร ก๊าซชีวภาพสะสมตลอดระยะเวลาการวิจัยที่ มีค่าเท่ากับ 103.2 ลิตร/กิโลกรัม น้ำหนักสดของวัสดุ และมีผลผลิตก๊าซชีวภาพ 3,325 ลิตร ปริมาณมีเทนสูงสุด 68.1% ดังนั้นการเพิ่มประสิทธิภาพการผลิตก๊าซชีวภาพด้วยความร้อนแสงอาทิตย์ โดยสามารถเพิ่มอุณหภูมิของวัตถุในถังหมักก๊าซชีวภาพเป็น 37 องศาเซลเซียส เป็นระยะเวลา 8 ชั่วโมง/วัน จากนั้น ได้ทำก๊าซชีวภาพให้บริสุทธิ์โดยการกรองคาร์บอนไดออกไซด์ที่มีอยู่ 16.5% ด้วยวิธีทางเคมีโดยใช้โซเดียมไฮดรอกไซด์ สามารถเพิ่มความเข้มข้นของมีเทนจาก 68.1% เพิ่มขึ้นเป็น 79.1% หลังจากการกรอง นอกจากนั้นยังได้วัดค่าความร้อนสูง (HCV) ซึ่งได้ค่าเท่ากับ 31.87 เมกะจูล/ลูกบาศก์เมตร และค่าความร้อนต่ำ (LCV) เท่ากับ 28.71 เมกะจูล/ลูกบาศก์เมตร ท้ายที่สุดได้ทำการวิเคราะห์ทางเศรษฐศาสตร์ คำนวณโดยใช้ต้นทุนเฉลี่ย หรือต้นทุนต่อหน่วยเท่ากับต้นทุนทั้งหมดหารด้วยจำนวนสินค้าที่ผลิต ดังนั้น ก๊าซชีวภาพที่ผลิตได้จากวิธีนี้เท่ากับ 14.03 บาท/ลูกบาศก์เมตร

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Author	Mr.Weerapong Pantumit
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ABSTRACT

Agricultural Thailand produces and exports Longan fruits. The industry in trading longan fruit is growing rapidly. This fruit has been widely cultivated, especially in northern Thailand. Longan production generates a huge amount of waste as well as after pruning such as leaves and stray branches. In this study, agricultural wastes (longan leaves) and pig manure substrates were used for biogas production. This research was divided into 3 parts. The first part was to evaluate the biogas production from longan leaves (*Dimocarpus longan*) with proximate analysis of C, H, O, N, and S content 47.33 %, 5.69%, 40%, 5.67%, and 0.23%, respectively. In addition, the longan leaves contained 9.61% moisture and 7.46% ash determined through dry weight. Total solids (TS), volatile solids (VS) and pH the determining with the result of 892,473 mg/kg, 833,384 mg/kg and 4.68 respectively. The biogas content were 43.66 % methane, 47.03% carbon oxide and 9.31% ammonia. Total biogas yield was 0.9068 m^3/kg achieved through theoretical estimation, and total methane yield reached 0.2081 m^3. In the second part, efficiency of pretreatment on longan leaves for biogas production co-digestion with pig manure was applied. Longan leaves pretreatment was accomplished through thermal pretreatment (hot water 100°C at with 2 h), chemical pretreatment (2%NaOH with 72 h), and physico-chemical (2%NaOH and kept at temperature 60°C by sola dryer with 72 h), by using ratio of longan leaves and pig manure at 10%TS (best ratio at 5:5 from RSM analysis). The cumulative biogas production yield by pretreatment thermal, chemical and physico-chemical pretreatment were 8,903 ml, 12,616 ml, and 13,221 ml, respectively. The methane contents were 54.5%, 60.1%, and 60.7%, respectively. In the third part, the best ratio and chemical pretreatment was used in the final experiment. This experiment showed the enhanced biogas production efficiency by solar heating experimental design using 200 L biogas production system with a working volume of 170 L. The accumulated biogas throughout the research period used 103.2 L/kg fresh material and received a 3,325 L biogas yield with 68.1% maximum methane content. Henceforth, the system can enhance biogas production efficiency by solar heating by increasing temperature of the substrate in the biogas digester at 37°C for 8 h/day. After which, biogas purification undergone a chemical process by NaOH and in order to remove 16.5 %. CO_2 content 68.1% CH_4 concentration increased to 79.1% after purification. High calorific value (HCV) was 31.87 MJ/m^3 and Low calorific value (LCV) was 28.71 MJ/m^3. The economic analysis calculation, calculated by using average cost or unit cost equal to the total cost divided by the number of goods produced; lasts of biogas produced with this method was 14.03 Baht/m^3.

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Weerapong Pantumit

June 2018

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ABBREVIATION

AD	Anaerobic digestion
Alk	Alkalinity
C/N	Carbon/Nitrogen
COD	Chemical Oxygen Demand
DM	Dry matter
e.g.	Exempli gratia
etc	The end of the sentence
h	Hour
HCV	Higher calorific values
LCV	Lower calorific values
MC	Methane content
NA	Not available
RSM	Response surface methodology
SD	Standard deviation
SEM	Scanning eletron microscopy
TS	Total solids
VFA	Volatile fatty acids
VS	Volatile solids
CCD	Central composite design

CHAPTER 1

INTRODUCTION

Statement of the problems

Thailand is an agricultural area suitaable for growing of various kinds of plants. One of these agricultural crops is Longan which has approximately 160,000 hectares plantation. Longan is one of the main economic subtropical fruits and most important fruit crop in Thailand. However, longan plantation produces large amount of wastes from its flowers and leaves which can be a source of biomass for the production of biofuel or biogas. Therefore, studying the energy production potential of longan leaves are very important (Auppathat et al., 2016).

Biogas is generated from anaerobic digestion process through biodegradation of organic matter. The main composition of biogas is 50-70% methane (CH_4), 30-40% carbon dioxide (CO_2), 5-10% hydrogen (H_2), 1-2% nitrogen (N_2), 100-3,000 ppm hydrogen sulphide (H_2S) and other. Methane is the main component of biogas as well as fuel. Biogas is considered as renewable energy and can be an alternative source of as electricity generation, and bio-methane gas production is useful for residential activities such as heating applications. The use of biogas as a renewable energy will be efficient and suitable for improving energy security anddecreasing environmental disruption caused by carbon emissions. Typical biogas production utilizes pig, cow and goat manure as raw material.However, in present studies, co-digestion of animal manure with agricultural waste was proven to improve the production of biogas (Li et al., 2015).

Co-digestion is the production of biogas by use animal manure and agricultural waste t through anaerobic digestion process. The co-digestion of animal manures and agricultural waste increases the nutrients of bacteria and the rate of biogas production due to nutrients and greater balance between carbon to nitrogen agricultural waste that improves anaerobic digestion efficiency.

Objectives

1. To estimate potential of longan leaves on biogas production.
2. To apply different pretreatment on longan leaves: chemical, physical and physico-chemical methods for producing biogas by co-digestion.
3. To apply the solar heating system to increase the temperature of a substrate in the fermenter to process biogas production.
4. To improves the quality of biogas by filtration using NaOH.

Benefits

1. Utilization of agricultural waste to produces energy security and decreasing environment pollution.
2. Can use as a model to increase revenue for people in local community from longan growing between output pending.

Scopes of study

1. Test biogas production by co-digestion of animal manure with longan leaves the mixing optimum ratio.
2. Test the concentration of NaOH in CO_2 filtration from biogas.

CHAPTER 2
LITERATURE REVIEW

Bio fuels

Biofuels is a term that commonly denotes liquid or gaseous fuels made from biomass. Based on the biomass resources used for biofuel conversion, they are classified as First generation biofuels and Second generation biofuels. Needless to say that with current global oil production approaching its peak, billions of tons of carbon emissions released into the atmosphere and threats of climatic change, it is obvious that clean energy is certainly an important scientific topic that needs special attention by the scientific community world-wide and, more so, in the context of the developing countries (Ullah et al., 2015).

Presently, about 87% of the global energy mix comes from depleting fuels and, with the exception of the nuclear energy (6%), all are carbon-rich fossil fuels such as oil (35%), natural gas (21%), and coal (25%); International Energy Agency (Taylor, 2010). The economically recoverable proven reserves of oil, natural gas, and coal represent at the end of 2007 about 41.6, 60.3, and 133 years, respectively, of supply at the current rate of consumption. Thus, a simple calculation shows that these proven reserves will be completely exhausted after 75 years at the current rate of consumption of fossil energy and most likely earlier considering the increasing worldwide energy demand (Ullah et al., 2015).

Biofuels can be classified based on their production technologies: first generation biofuels (FGBs); second generation biofuels (SGBs); third generation biofuels (TGBs); and fourth generation biofuels. Table 1 shows the classification of renewable biofuels based on their production technologies (Fatih Demirbas, 2009).

Table 1 Classification of renewable biofuels based on their production technologies.

Generation	Feedstock	Example
1^{st} generation biofuels	Sugar, starch, vegetable oils, or animal fats	Bioalcohols, vegetable oil, biodiesel, biosyngas, biogas
2^{nd} generation biofuels	Non-food crops, wheat straw, corn, wood, solid waste, energy crop	Bioalcohols, bio-oil, bio-DMF, biohydrogen, bio-Fischer–Tropsch diesel, wood diesel
3^{rd} generation biofuels	Algae	Vegetable oil, biodiesel
4^{th} generation biofuels	Vegetable oil, biodiesel	Biogasoline

First generation biofuels (FGBs) refer to biofuels made from sugar, starch, vegetable oils, or animal fats using conventional technology. FGBs produced from food crops such as grains, sugar beet, and oil seeds are limited in their ability to achieve targets for oil-product substitution, climate change mitigation, and economic growth. A possible exception that appears to meet many of the acceptable criteria is bioethanol produced from sugar cane. The basic feedstocks for the production of first generation biofuels are often seeds or grains such as wheat, which yields starch that is fermented into bioethanol, or sunflower seeds, which are pressed to yield vegetable oil that can be used in biodiesel.

The production of FGBs such as sugarcane ethanol in Brazil, corn ethanol in US, oilseed rape bio-diesel in Germany, and palm oil biodiesel in Malaysia is characterized by mature commercial markets and well understood technologies. Future targets and investment plans suggest strong growth will continue in the near future (Thamsiriroj, 2009).

Second generation biofuels (SGBs) produced from (larger) feedstocks from lignocellulosic materials include cereal straw, forest residues, bagasse, and purposegrown energy crops such as vegetative grasses and short rotation forests. The SGBs could avoid many of the concerns facing FGBs and potentially offer greater cost reduction potential in the longer term. Many of problems associated with FGBs can be addressed by the production of biofuels manufactured from agricultural and forest residues and from non-food crop feedstocks. Low-cost crop and forest, wood process wastes, and the organic fraction of municipal solid wastes can all be used as lignocellulosic feedstocks. Second and third generation biofuels are also called advanced biofuels. Second generation biofuels are made from non-food crops, wheat straw, corn, wood, energy crop using advanced technology. Algae fuel, also called oilgae or third generation biofuel, is a biofuel from algae. On the other hand, an appearing fourth generation is based in the conversion of vegoil and bio-diesel into biogasoline using most advanced technology (Hilal Demirbas, 2009).

Main thermochemical conversion processes are pyrolysis, gasification, and liquefaction. Biorenewable feedstocks can be converted into liquid or gaseous forms for the production of electric power, heat, chemicals, or gaseous and liquid fuels. Figure 1 shows an overview of conversion routes of plant materials to biofuels. Biogas is one of increase renewable energy production from lignocellulose biomass to replace fuels (Fatih Demirbas, 2009).

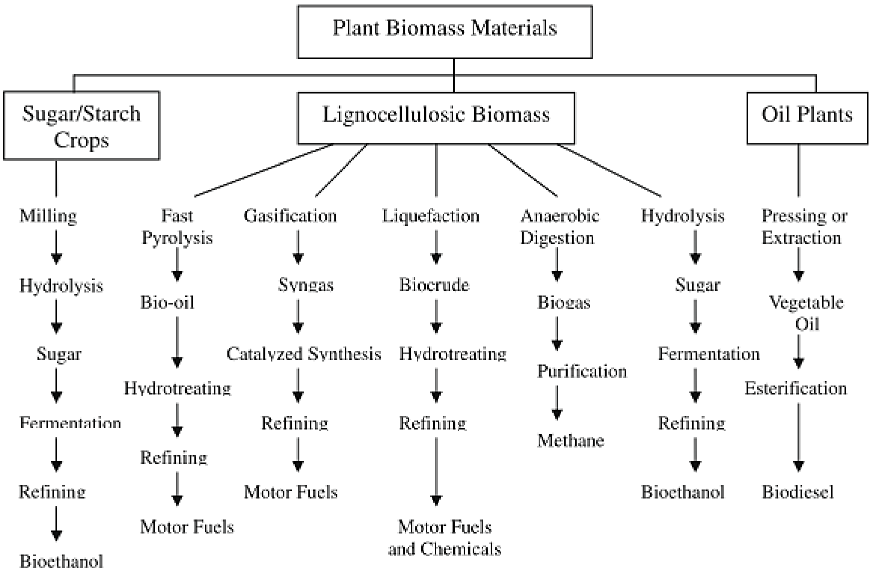

Figure 1 Overview of conversion processes of plant materials to biofuels.

Biomass and biogas energy in Thailand

Biomass is an important source of renewable energy in Thailand and currently is the second major energy sources in the country, especially for households and small industries in rural area. It provides basic energy requirement for cooking and process heating in residential and manufacturing sectors as well as for processing in traditional industries. Four major sources of biomass in Thailand are sugar cane, rice, oil palm and wood wastes which yield a total potential of nearly 80 million tons per year. At present, agro-industry is an important source of the biomass due to a large-scale production and expedience collection such as rice mills, sugar mills, and oil palm mills (Seksan et al., 2004). The major biomass resources in Thailand include the following (Hanekamp, 2014):

- Agricultural residues (rice husk, bagasse, corn cobs, etc.)
- Wood residues from wood and furniture industries (bark, sawdust, etc.)
- Biomass for ethanol production (cassava, sugar cane, etc.)
- Biomass for biodiesel production (palm oil, jatropha oil, etc.)
- Industrial wastewater from agro-industry
- Livestock manure
- Municipal solid wastes and sewage

Since Thailand is the agricultural base country, there are a lot of agricultural crops, e.g. paddy rice, sugarcane, cassava and palm oil. During the harvesting and processing of these agricultural crops, some residues are left over, e.g. rice straw and rice husk from paddy rice, bagasse and sugarcane leave from sugarcane, cassava rhizome from cassava as well as palm oil shell, palm oil fiber and palm oil empty fruit bunch from palm oil fruit. These residues can further be used as the substitute to fossil fuel for energy production and, consequently, can solve the problem of high energy price as well as global warming (Kerdsuwan and Laohalidanond, 2011). Table 2 shows the amount of residues and energy potential from domestic main agricultural products based on productivity in 2009 (Kerdsuwan and Laohalidanond, 2011).

Table 2 Energy potential of main agricultural residues in Thailand.

Agricultural product	Residues	Productivity (kton)	Quantity of residues (kton)	LHV (MJ/kg) (Prasertsan & Sajjakulnukit, 2006)	Total Energy (PJ)
Paddy rice		32,116			
	Rice husk		3,641.63	14.27	51.97
	Rice		9,819.40	10.24	100.55
Sugarcane	straw	68,808			
			4,545.25	8.31	37.77
	Bagasse		20,489.10	8.70	178.26
Cassava	Sugarcan	22,006			
	e leaves		10,567.28	5.50	58.12
Palm oil		8,223			
fruit	Cassava		14.91	18.46	0.28
	rhizome		161.98	17.62	2.85
			1,200.56	17.86	21.44
	Shell		21,412.69	9.83	210.49
	Fiber				
	Empty				
	fruit				
	bunch				
	Frond				
Total					661.73

From Table 3, the energy potential of agricultural residues generated from four main agricultural products in 2009 was accounted for 661.73 PJ. The utilization of agricultural residues bunch as renewable energy. Since Thailand has spent a large amount of money for importing commercial energy sources, Thai government as well as private and public organizations have realized about that, Ministry of Energy of

Thailand has promoted the use of renewable energy, including biomass, municipal solid waste, biogas, wind and solar power for power generation or transportation fuel production by announcing the 15-Years of Alternatives Energy Development Plan (AEDP, 2009) on January 28, 2009 (Kerdsuwan and Laohalidanond, 2011). The objective of this AEDP is to strengthen and promote the utilization of renewable energy in order to replace the oil import. The main target of AEDP is to increase the portion of using alternative energy to 20 % of national final energy consumption by 2020. The plan will be implemented into three phases: short-term from 2008 to 2011, mid-term from 2012 to 2016 and long-term from 2017 to 2020. From Table 3, it can be noticed that the main target of AEDP until 2020 is the utilization of biomass for electricity and heat production.

Table 3 15-Years of alternatives energy development plan (AEDP, 2009).

Energy Electricity	**Potential (MW)**	**Existing (MW)**	**2008-2011 (MW)**	**2012-2016 (MW)**	**2017-2020 (MW)**
Solar	50,000	32	55	95	500
Wind	1,600	1	150	400	700
Hydro	700	50	165	281	324
Biomass	4,400	1,597	2,800	3,235	3,700
Biogas	190	29	60	90	120
MSW	320	5	100	130	160
Hydrogen	-	-	0	0	3.5
Heat	ktoe	ktoe	ktoe	ktoe	ktoe
Solar	154	2.3	5	17	34
Biomass	7,400	2,344	3,544	4,915	6,725
Biogas	600	79	470	540	600
MSW	78	1	16	25	35
Biofuels	Ml/day	Ml/day	ktoe	ktoe	ktoe
Ethanol	3.30	1.00	816	1,686	2,447
Biodiesel	3.30	1.39	944	1,145	1,416
Hydrogen	-	-	0	0	124

In addition to electricity and heat, biomass can also be used as feedstock for biofuel production. So, Ministry of Energy determined Alternative Energy Development Plan (AEDP 2012-2021) aims to achieve 25% of energy consumption from renewable by 2021. Biogas is one of this plan for increase renewable energy production to replace fuels in the country (Tonrangklang et al., 2017). The overall number of plants might vary, since there might have been double counting of plants from different phases. In addition, plants that are not supported are not monitored. Currently, as can be seen in Table 4, the largest amount of biogas plants is installed in the livestock sector (EPPO, 2013).

Table 4 Biogas plants in Thailand.

Industry sector	Number of plants	Biogas production in Mio m^3/a
Pig farms (subsidy phases I-III, 1995-2010)	271	88.6
Pig farms (2008-2012)	263	74.81
Small agricultural operations	575	9.51
Slaughterhouses (pigs)	12	0.74
Slaughterhouses (poultry)	5	6.02
Cassava starch	59	385.82
Palm oil	88	211
Ethanol	21	263.05
Caoutchouc	7	2.08
Foodstuff residues	47	51.27
Catering waste from hotels etc.	80	2.28
Others	140	427.37
Total	1,568	1,522.55

Biogas production by anaerobic digestion

Biogas production from process of biodegradation of an organic matter by anaerobic bacteria in the absence state of oxygen. The product realization after of a process anaerobic digestion namely biogas. The main composition of biogas is 50-70% methane (CH_4), 30-40% carbon dioxide (CO_2), 5-10% hydrogen (H_2), 1-2% nitrogen (N_2), 100-3,000 ppm hydrogen sulphide (H_2S) and other. The most important biogas that can light a fire is CH_4. The typical biogas composition ranges, irrespective of substrate used in the AD process, are noted in Table 5.

Table 5 Typical composition of biogas.

Substance	Formula	Percentage (%)
Methane	CH_4	50-80
Carbon Dioxide	CO_2	20-50
Hydrogen	H_2	5-10
Nitrogen	N_2	1-2
Water Vapour	H_2O	0.3
Hydrogen Sulphide	H_2S	Traces

Biochemical process of anaerobic digestion

The breakdown of complex organic matter in an anaerobic process involves multiple steps, which are carried out by several groups of microorganisms. The end product of anaerobic degradation of organic compounds is biogas, an energy-rich gas mixture consisting of mainly CH_4 and CO_2. Figure 2 shows the schematics of various steps and microbial groups involved during AD. Contains examples of some different groups of extracellular enzymes. Each group contains several enzymes that are specialized in various substrates, such as different proteins. The rate of decomposition during the hydrolysis stage depends greatly on the nature of the substrate. The transformation of cellulose and hemicellulose generally takes place more slowly than the decomposition of proteins (Adekunle and Okolie, 2015). Some of the important biochemical process of anaerobic digestion are presented in the following sections.

Hydrolysis

Biodegradation from a complex organic compound become organic monomer by extracellular enzyme from anaerobic bacteria. The cleavage of chemical bonds by the addition of water such as carbohydrate polysaccharides (complex sugars) are broken down into monosaccharides. One example is the breakdown of lactose into galactose and glucose, Triglycerides are split into three fatty acids and glycerol by the addition of three water molecules, proteins, peptide bonds are broken to separate amino acids.

Acidogenesis

The Second step in the anaerobic digestion process. Acidogenesis is the volatilefatty acid production from acidogenic bacteria activities use organic monomer nutrients for growth. The acidogenic bacterial activity is organic monomer into volatilefatty acid molecule not more than 5 atoms such as acetic acid, formic acid, propionic acid, isobutyric acid, valeric acid, isovaleric acid, butyric acid.

Acetogenesis

The third step in the anaerobic digestion process. Acetogenesis is an acetate and formate production process from acetogenic bacteria by acetogenic bacteria consume precursors and produce acetate and formate. The acetate and formate is an important component in to create CH_4.

Methanogenesis

The final step of anaerobic digestion process. Methanogenesis is the formation of methane from methanogens bacteria by use an acetate and formate in the formation of methane.

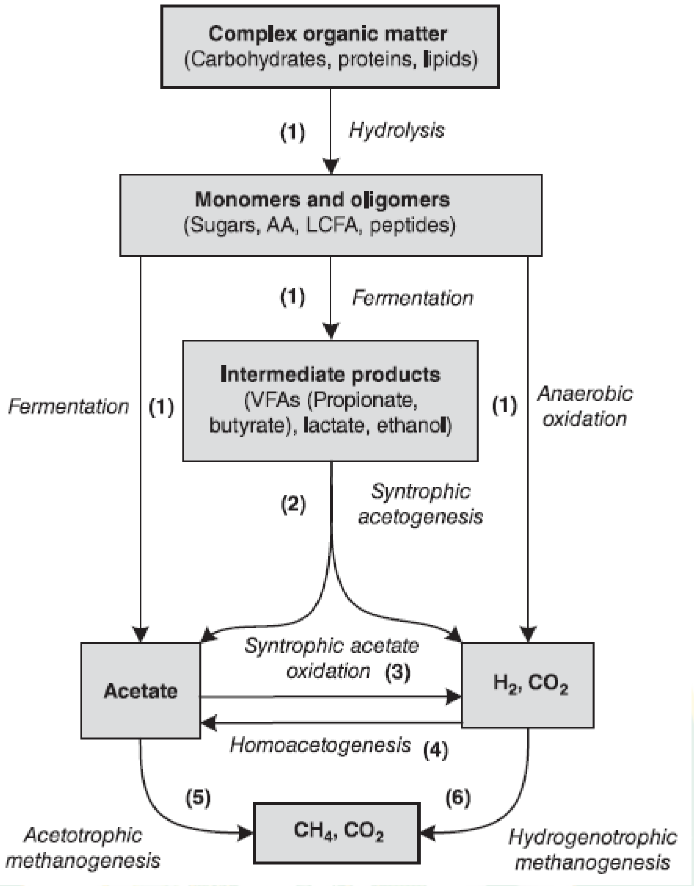

Figure 2 Stages of anaerobic digestion 1. Fermentative bacteria; 2. Acetogenic bacteria; 3. Syntrophic acetate oxidizing bacteria; 4. Homoacetogens; 5. Acetotrophic methanogens; 6. Hydrogenetrophic methanogens. Notes: AA: amino acids; LCFA: long-chain fatty acids; VFAs: volatile fatty acids. (Khanal, 2008)

Other parameters that Influence biogas production

Since biogas production from an anaerobic digester consist the bacterial activity thus factors biogas production depends on the ability of bacteria to thrive inside the digester such as Temperature. (Rea, 2014)

Temperature

Anaerobic processes, like most other biological processes, are strongly dependent on temperature. Although anaerobic microorganisms, especially methanogens, are viable at different temperatures, methanogens are accordingly classified as psychrophiles, mesophiles, and thermophiles. The anaerobic conversion rates generally increase with temperature up to 60°C. There are three anaerobic digestion in temperature ranges, mesophilic digestion occurs between 25-45°C, psychrophilic digestion occurs at below 25°C, or below room temperature and thermophilic digestion occurs above 45°C. In general, higher temperatures result of higher biogas production Also, rapid temperature changes can upset bacterial activity, so for experimental studying, temperature Control is important that temperature is held constant (Rea, 2014). As shown in Figure 3 (Lettinga et al., 2001; van Haandel and Lettinga, 1994) a rule of thumb, the biological activity doubles for every 10°C increase in temperature within the optimal temperature range.

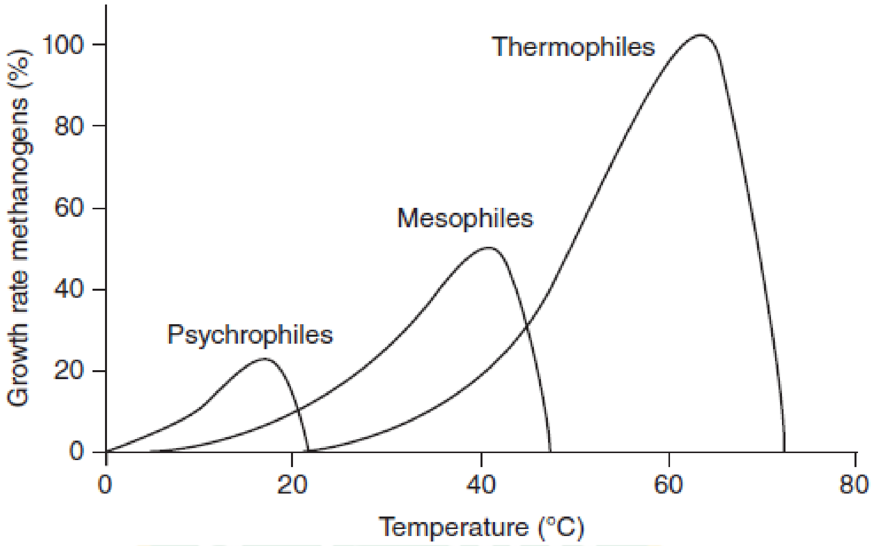

Figure 3 Relative growth rate of psychrophilic, mesophilic, and thermophilic methanogens. (Lettinga et al., 2001)

Figure 4 shows the effects of temperature on the activities of mesophilic methanogens. As evident from the graph, methanogens have the highest activity at around 35°C. It is, however, not uncommon to see a full-scale anaerobic digester operating at a mesophilic temperature of 40-45°C

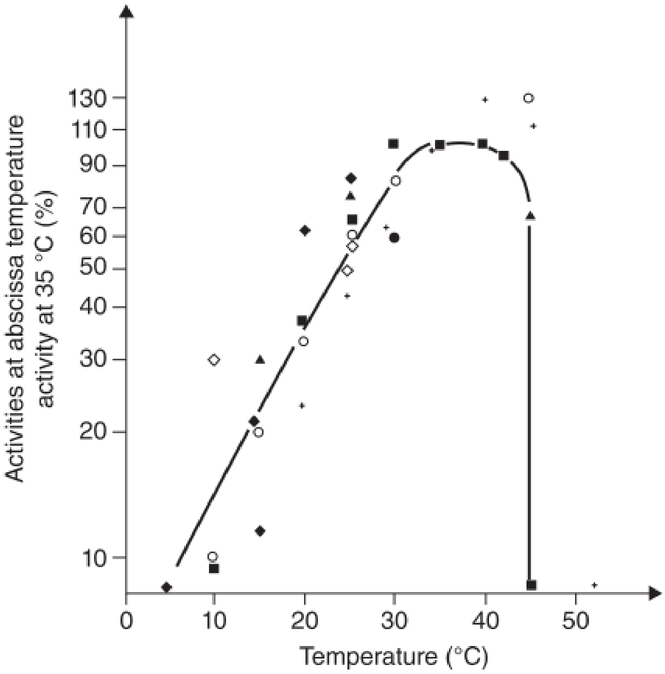

Figure 4 Activities of mesophilic methanogens at different temperatures.

pH and Alkalinity

Methanogens bacteria are sensitive bacteria to pH changes as possible by step of methanogenesis process will happen at pH 6.8-7.0 and optimum pH at 7.0 and the optimum pH is 5.5-6.5 for acidogens. Since methanogenesis is often considered to be the rate-limiting step in AD, it is necessary to maintain the digester pH close to neutral. Acidogens are significantly less sensitive to low or high pH values and acid fermentation prevails over methanogenesis, which may result in souring of the reactor contents (van Haandel and Lettinga, 1994). When the decreases pH lower than 6.2 resulting in production of biogas decreases (Rea, 2014). Methanogenic activity (i.e., the acetate utilization rate) versus pH is shown in Figure 5. This clearly demonstrates that the highest methanogenic activity occurs around a neutral pH range.

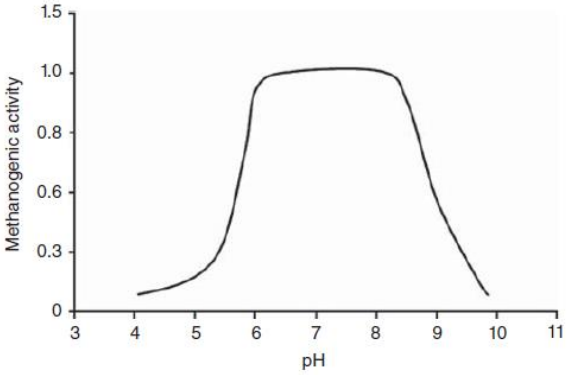

Figure 5 pH dependence of methanogenic activity. (Khanal, 2008)

Alkalinity is affected by the composition of feedstocks, which thereby affects the digester pH. The alkalinity and pH of AD may change substantially due to the degradation of substrates. Degradation of protein produces ammonia and results in an increase in alkalinity, while degradation of carbohydrates and fats produces organic acids that consume the alkalinity, thereby lowering the pH. Alkalinity supplementation in the digester to maintain an optimum pH is carried out using chemicals such as sodium bicarbonate, sodium carbonate, ammonium hydroxide, and lime (Li and Khanal, 2016).

Volatile fatty acids

VFA are some of the most important intermediates in the anaerobic biogas process; it is the conversion from VFA into methane and carbon dioxide which is important. The increase of VFA concentration in the biogas process is well-known, as a result of process imbalance. Thus, it has been commonly suggested as an indicator in the anaerobic digester (Lo Niee Liew, 2011). VFAs are produced by the acetogens and consumed by the methanogens, and if the inhibition of methanogens occurs, there would be a buildup of VFAs. The accumulation of VFA leads to a pH drop wherein the whole digester could stop working and activity of methanogens was inhibited to a significant extent. Some studies have found that propionic acid should be treated as a toxic volatile fatty acid in anaerobic digester and the methanogenic bacteria have been shown vulnerable to propionic acid concentration greater than 1,000-2,000 mg/L (Lee et al., 2015).

Nutrient

Efficient biodegradation requires nutrients and sufficient nutrients are therefore important to microbial cell growth. Which in the biogas process are chemical compounds such as proteins, fats, or carbohydrates. Furthermore, they require an electron acceptor, mainly CO_2 for the anaerobic digester. Nutrient supplementation can be calculated based on the nutrients required for biomass synthesis by assuming the empirical formula of the microbial cells as $C_5H_7O_2N$ (Speece and McCarty, 1964). Macro nutrients such as carbon, nitrogen, potassium phosphorus, sulphur (Kayhanian and Rich, 1995) and micro-nutrients such as Fe, Ni, Zn and Co in smaller amount (Cresson et al., 2006) are required for optimal anaerobic microbial growth. For a highly loaded (0.8–1.2 kg COD/(kg VSS day)) AD system, the theoretical minimum COD : N : P ratio of 350 : 7 : 1 is recommended, whereas for a lightly loaded (<0.5 kg COD/ (kg VSS day)) AD system, the recommended COD : N : P ratio is 1,000 : 7 : 1 to calculate the nitrogen and phosphorus needs (Henze and Harremöes, 1983). For AD of high-solids feedstocks such as lignocellulosic biomass, food wastes and animal manures nutrient requirements are often estimated based on the carbon-to-nitrogen (C/N) ratio. The recommended C/N ratio for high-solids AD is 20-30, with 25 being the optimal. Co-digestion of high-carbon feedstocks such as fiber-rich biomass with high-nitrogen feedstocks such as animal manures is a good strategy to fulfill the nutrient requirements. Typical C/N ratios of some common feedstocks are shown in Table 6 (Li and Khanal, 2016).

Table 6 Carbon-to-nitrogen (C/N) ratios for selected feedstocks.

Feedstocks	C/N ratio
Kitchen waste	14-16
Chicken manure	5-15
Swine manure	10-20
Dairy manure	10-15
Corn silage	30-50

Toxic materials and Inhibition

The AD process is highly susceptible to toxic substances. The toxic substances are present in either the influent or the byproducts of the metabolic activities of the microorganisms. Heavy metals, halogenated compounds, cyanide, phenol, and so on are examples of the former, while ammonia, sulfide, and long-chain fatty acids belong to the latter group. Non-ionized sulfide, ammonia, and VFAs are more toxic to anaerobic microbes, especially methanogens, than their ionized forms. The relative distribution of ionized and non-ionized forms is governed by the operating pH, with alkaline pH favoring the more ionized form of these compounds. Soluble heavy metals are regarded as more critical to failure of an AD system than insoluble forms (Stronach et al., 1986). An inhibition of ammonia on the methanogens leads to the accumulation of volatile fatty acids (VFA). VFAs are produced by the acetogens and consumed by the methanogens, and if the inhibition of methanogens occurs, there would be a buildup of VFAs (Teghammar, 2013). The generation of sulfide benefits AD by reducing metal toxicity through the formation of insoluble metal sulfides, with the exception of chromium (Cr). Approximately 0.5 mg of sulfide is needed to precipitate 1.0 mg of heavy metal. Heavy metal toxicity follows the following order: Ni > Cu > Pb > Cr > Zn (Hayes and Theis, 1978), with Fe considered more beneficial than detrimental because it mediates sulfide toxicity. Acclimation to toxic compounds is a key feature to reduce the inhibitory effect on anaerobic microbes. Digesters with a long SRT, high biomass inventory, and biofilm/UASB are more tolerant to toxic compounds (Li and Khanal, 2016).

Total solids content

The anaerobic process for low TS content is mainly employed for wastewater treatment coupled with bioenergy production. AD at up to 15% TS content is categorized as liquid/wet digestion, and is carried out in a continuous-stirred tank reactor (CSTR). Examples of such feedstock include animal manure, lignocellulosic biomass, food-processing waste, food waste, sewage sludge, biofuel residues etc. In solid-state digestion, the TS content is >15% and is often around 20-25%. OFMSW is digested at very high TS contents (20-40%) and is commonly known as dry digestion.

Dry digestion is attractive because the quantity of water generated from the digester is substantially low and, consequently, reduces the digester size significantly. The volumetric methane production rate during AD often increases with the increase in TS content until a threshold TS content of 15-20% is reached (Figure 6). The increase in the volumetric methane production rate is mainly associated with the increase in substrate availability for microbial growth, while the decrease in the volumetric methane production rate is mainly caused by the mass diffusion limitation at high TS levels (Xu et al., 2014).

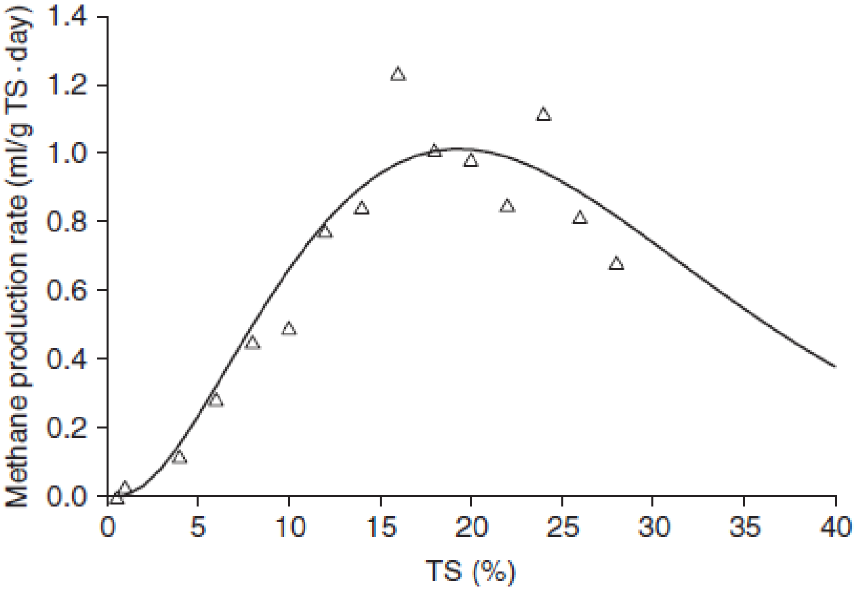

Figure 6 Effect of TS content on volumetric methane production rate. (Xu et al., 2014)

Anaerobic digestion systems

One of the important considerations in anaerobic digester design is microbial biomass retention capacity, because anaerobic bacteria, especially methanogens, grow slowly. Thus, it is essential to maintain a long solids retention time (SRT), irrespective of hydraulic retention time (HRT) (Li and Khanal, 2016). Such decoupling can maintain a significantly high SRT/HRT ratio, which prevents the washout of slow-growing anaerobes, especially methanogens. Some of the approaches of decoupling are biomass immobilization in attached growth systems; granulation and floc formation; biomass recycling; and biomass retention. For dilute substrates (e.g., wastewaters), decoupling is extremely important and is achieved through one of the approaches already discussed. Decoupling is extremely difficult for high-solids substrates, which are often employed for bioenergy production in AD. Such feedstocks are frequently digested in a completely mixed reactor commonly known as continuous-stirred tank reactor (CSTR), in which HRT = SRT (Li and Khanal, 2016). Based on this discussion, an AD system can be classified into two broad categories, namely, suspended growth and attached growth systems, as shown in Figure 7.

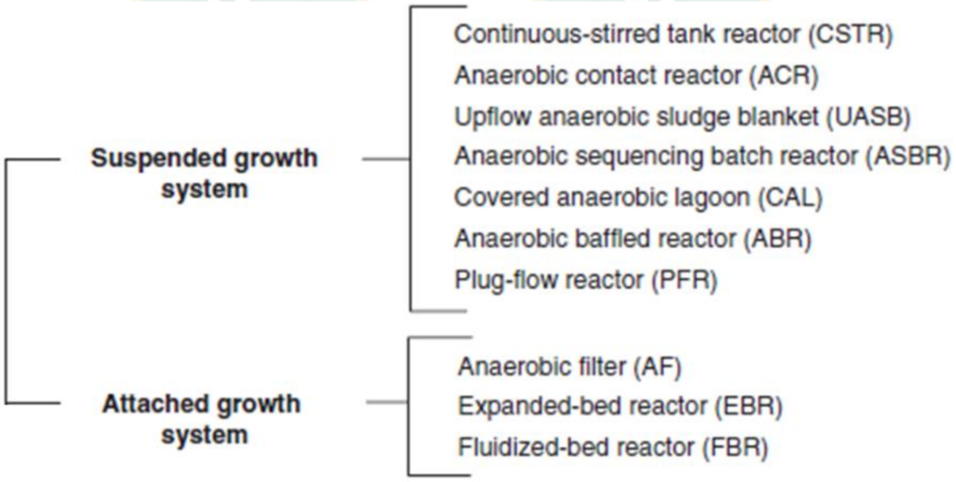

Figure 7 Classification of anaerobic digestion systems. (Li and Khanal, 2016)

Suspended growth systems

The majority of anaerobic reactors currently in operation are suspended growth systems, in which microbes are in suspension in the reactor. The mixing action distributes the bacteria throughout the digester. Advantages and disengages of suspended growth anaerobic digester are listed in Table 7 (Gerardi, 2003). Some of the important suspended growth reactors are presented in the following Table 8 (Li and Khanal, 2016).

Table 7 Advantages and disengages of suspended growth anaerobic digester.

Advantages	- Suitable for the treatment of particulate, colloidal, and soluble wastes. - Toxic wastes may be diluted. - Uniform distribution of nutrients, pH, substrate, and temperature.
Disadvantages	- Large digester volume required to provide necessary SRT. Treatment efficiency may be reduced due to loss of particulate and colloidal waste and bacteria in digester effluent.

Table 8 Detail of suspended growth anaerobic digester.

Digester	Detail	HRT
Continuous-Stirred Tank Reactor (CSTR)	The contents in the reactor are completely mixed by intermittent or continuous stirring. Thus, the concentrations of all constituents are nearly the same throughout the reactor and in the digestate (effluent). Since the substrate (influent) gets diluted rapidly in the reactor, a CSTR is less sensitive to shock loading or toxicity.	20-50 Day
Upflow Anaerobic Sludge Blanket (UASB) Reactor	Are essentially a suspended growth system in which proper HRT/OLR is maintained in order to facilitate the dense biomass aggregation known as granulation. The size of the granules is about 1-3 mm diameter. Since the granules are large in size and dense, they settle and are retained within the reactor. The volatile suspended solids (VSS) concentration in the reactor may go as high as 50 g/L.	4-8 h
Plug-Flow Digester	A relatively simple and low-cost reactor configuration. Consist of a long rectangular concrete tank or polyethylene tube. The tank is sealed with a hard (concrete) or flexible (polypropylene) cover. Do not have any mixing device and are mostly operated at mesophilic (35-37°C) conditions.	15-30 day

Covered Anaerobic Lagoon	Widely adopted as a low-cost option for digesting/stabilizing waste streams with a TS content of 0.5-3%, such as flushed dairy manure, swine manure, or industrial wastewater. Lagoons are earthen structures/pits constructed with impermeable liners such as clay or plastic at the bottom and sides to prevent liquid seepage. Since lagoons are operated at ambient temperature, their digestion efficiency and biogas production are strongly dependent on geographical location and climate.	3-6 months

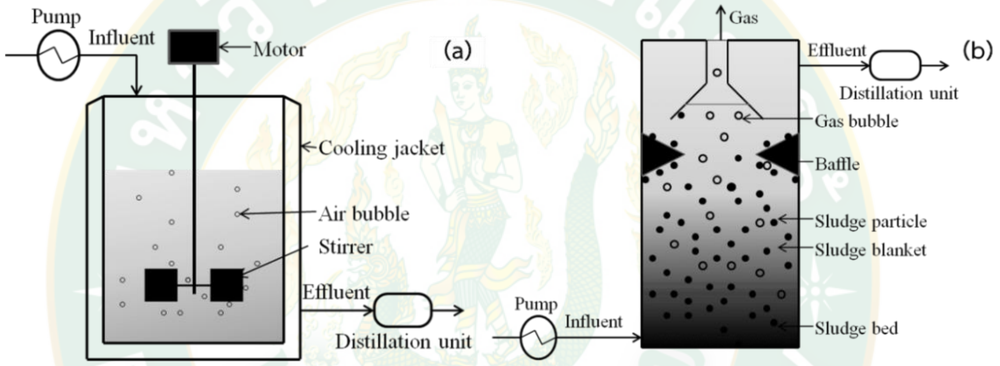

Figure 8 Schematic diagram of a (a) Continuous-stirred tank reactor (CSTR) (Bhatia and Yang, 2017) and (b) UASB reactor (Khanal, 2008).

In addition another suspended growth anaerobic digester such as Anaerobic Contact Reactor (ACR) is essentially a completely mixed digester coupled with a downstream settling tank. The settled microbial biomass is recycled back to the digester. Hence ACR is able to maintain a high concentration of microbial biomass in the digester; Anaerobic Baffled Reactor (ABR) the substrate flows over and under the baffles. The microbial biomass accumulates between the baffles and may in fact form granules with time. The baffles prevent the horizontal movement of biomass in the reactor. Thus, a high concentration of microbes is achieved; Anaerobic Sequencing Batch Reactor (ASBR) was developed as a high-rate anaerobic reactor to treat high-strength and medium solids content feeds (TS: 1-4%) in Figure 8.

Attached growth systems

An attached growth system, also known as a biofilm system, is a high-rate anaerobic system in which anaerobic microorganisms, especially methanogens, get attached to an inert media through self-immobilization. Different inert media or bio carriers such as crushed rock, tiles and plastic of different shapes are used for microbial attachment. These media usually have a very high surface area, which facilitates biofilm formation. Thus, an attached growth anaerobic system maintains a very long SRT independent of HRT. Advantages and disengages of attached growth anaerobic digester are listed in Table 9 (Loupasaki and Diamadopoulos, 2013). Some examples of attached growth anaerobic systems are discussed in the following sections.

Anaerobic filter (AF)

Depending on feeding mode, an anaerobic filter is classified as an upflow anaerobic filter (UAF; Figure 9a), a downflow anaerobic filter (DAF; Figure 9b), or a multifed anaerobic filter (MFAF; Figure 9c). In a UAF, substrate flows upward through a media bed and the entire bed is submerged. The non-attached microbial biomass forms a bigger floc and eventually takes a granular shape due to the rolling action of rising biogas bubbles. Thus, non-attached biomass contributes significantly to biological activity. The biofilm growth on support media in a UAF is shown in Figure 9a (Li and Khanal, 2016). A DAF, loosely held biomass in a DAF gets washed out of the reactor. The specific surface area of the media plays a more important role in a DAF than in a UAF. Clogging is less of a problem with a DAF, and it can accommodate feed streams with some suspended solids. Although a DAF has a low biomass inventory, the specific activity of its biomass is relatively high. In a MFAF, the feed enters the bioreactor through several points along the filter depth. The MFAF maintains a completely mixed regime throughout the reactor, preventing short-circuiting and accumulation of VFAs. In a MFAF substrate is uniformly distributed throughout the reactor, which prevents heavy microbial growth at the bottom of the reactor and minimizes clogging of the bed.

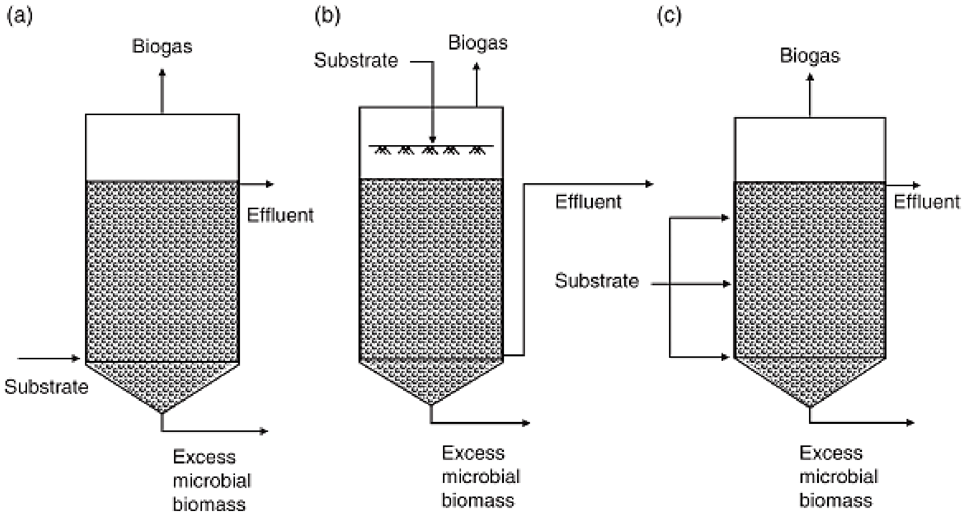

Figure 9 Schematic diagram of anaerobic filters: (a) upflow anaerobic filter, (b) downflow anaerobic filter, and (c) multifed anaerobic filter (Khanal, 2008).

Expanded bed reactor (EBR)

An EBR is an attached growth system with some suspended biomass. The microbes get attached on biocarriers such as sand, activated carbon, pulverized polyvinyl chloride, and shredded tire beads. The biocarriers are expanded by the upflow influent velocity and recirculated effluent. In expanded bed reactors, sufficient upflow velocity is maintained to expand the bed by 15-30%. The expanded bed reactor has fewer clogging problems and better substrate diffusion within the biofilm. The biocarriers are partly supported by fluid flow and partly by contact with adjacent biocarriers, and they tend to remain at the same relative position within the bed (Figure 10a).

Fluidized bed reactor (FBR)

Although an FBR is similar to an EBR in terms of configuration, an FBR is truly a fixed film reactor, as the suspended microbial biomass is washed out due to the high upflow liquid velocity. The bed expansion is 25-300% of the settled bed volume, which requires a much higher upflow velocity (10-25 m/h). The biocarriers are supported entirely by the upflow liquid velocity and are therefore able to move freely in the bed

(Figure 10b). The FBR is free from clogging and short-circuiting problems and results in better substrate diffusion within the biofilm.

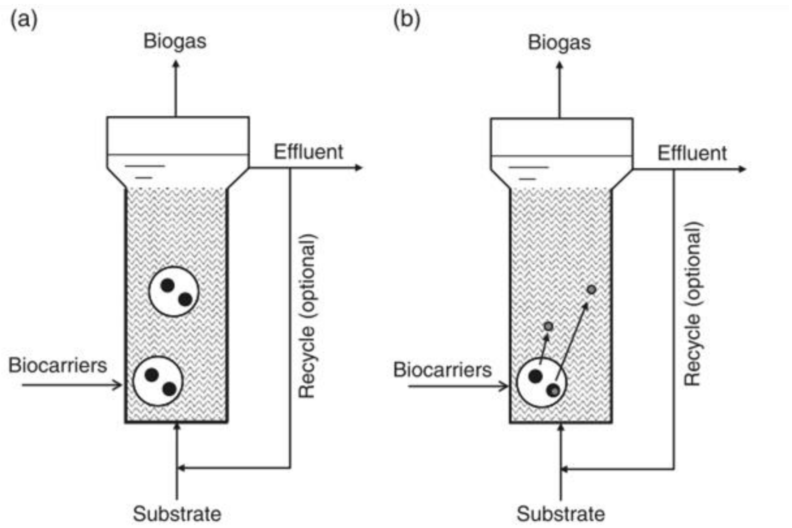

Figure 10 Schematics of (a) an expanded bed reactor and (b) a fluidized bed reactor.

Table 9 Advantages and disengages of attached growth anaerobic digester.

Advantages	- Maintain a high concentration of microorganisms resulting in high removal rates at relatively small hydraulic retention times. - Relatively short hydraulic retention times, high removal rates.
Disadvantages	- Large land requirement, odor issues associated with clogging of certain media, and the inability to handle high volumes of biofilm on media.

Lignocellulosic biomass

Lignocellulosic biomass mainly consists of three types of polymers: cellulose, hemicellulose, and lignin (Table 10) (Teghammar, 2013). The carbohydrate components (cellulose and hemicellulose) are fermentable after hydrolysis, which makes lignocellulosic biomass a suitable feedstock for bioenergy production. However, the inherent characteristics of native lignocellulosic biomass, such as structural and chemical properties, make it resistant to biodegradation by enzymes and microbes.

Table 10 Composition of the three main lignocellulose groups, expressed as % of original dry matter.

	Softwood1 (spruce)	**Hardwood1 (beech)**	**Grass2 (switchgrass)**
Cellulose	44.7%	45.6%	32.2%
Hemicellulose	22.9%	25.9%	24.4%
Lignin	30.6%	23.8%	23.2%
Others	1.8%	4.7%	20.2%

Cellulose is the main component of lignocellulose cell walls. It is a linear polysaccharide polymer of cellobiose (glucose disaccharide) strongly linked via β-1, 4 glycosidic linkages. A number of hydroxylic groups are present in the cellulose chains, leading to the formation of hydrogen bonds in the same chains or in vicinal chains. Cellulose molecules have different orientations throughout the structure, leading to different levels of crystallinity. Thus, cellulose consists of two regions: amorphous (low crystallinity) and crystalline (high crystallinity) region (Zheng et al., 2014). The crystallinity of cellulose can be characterized by the crystallinity index. The higher the crystallinity index, the more difficult the biodegradation of cellulose becomes. Meanwhile, cellulose microfibrils are also attached to each other by hemicellulose and/or pectin, and covered by lignin. Such a specialized and complicated structure renders cellulose resistant to biological and chemical attacks.

In contrast to cellulose, hemicelluloses are more amorphous, random, and branched heterogenic polysaccharides of various pentoses (xylose and arabinose), hexoses (glucose, galactose, mannose, and/or rhamnose), and acids (glucuronic acid, methyl glucuronic acid, and galacturonic acid). Short and branched chains of hemicelluloses help build a network with cellulose microfibrils and interact with lignin, rendering the cellulose-hemicellulose-lignin matrix extremely rigid. The amorphous and branched properties make hemicelluloses highly susceptible to biological, thermal, and chemical hydrolysis of their monomer compound (Zheng et al., 2014).

Moisture content, pH, and temperature are critical parameters in thermo-chemical hydrolysis of hemicellulose (Zheng et al., 2014).

After cellulose, lignin is the second most abundant organic compound in nature. It is a large and complex aromatic and hydrophobic amorphous heteropolymer and is constructed of phenylpropane units such as coniferyl alcohol and sinapyl alcohol with hydroxyl, methoxyl, and carbonyl functional groups (Zheng et al., 2014). Lignin plays the role of cement for the cross-linking between cellulose and hemicellulose to form a rigid three-dimensional structure of the cell wall (Zheng et al., 2014). It is also water insoluble and optically inert. Lignin has been shown to dissolve in water at high temperature (e.g. 180°C), neutral pH, or acid/alkaline conditions depending on the precursors of the lignin (Zheng et al., 2014). These properties of lignin make it the most recalcitrant component of the plant cell wall, and the higher the lignin content, the greater the resistance of the biomass to chemical and biological degradation. Lignin is a major barrier to utilization of lignocellulosic biomass in bioconversion processes. In general, softwood contains more lignin than hardwood and most agricultural residues, so that softwood is generally the most recalcitrant to pretreatment and bioconversion.

Lignocellulosic structure are there higher plants consist of two types of cell walls, primary and secondary. The primary wall is the outermost wall and is usually not lignified. The primary cell wall provides mechanical strength but also flexibility during the growth of the cell. The secondary wall is constructed inside the primary cell wall when the cell is mature and fully expanded. The secondary cell wall is thicker and stronger and contains a large amount of lignin. It is often divided into three layers (S1, S2 and S3) and the cellulose fibers in each layer are sorted in different directions compared to the other layers (Figure 11). The secondary cell wall accounts for most of the carbohydrates in biomass. The space between the cells, called the middle lamella, is often also lignified

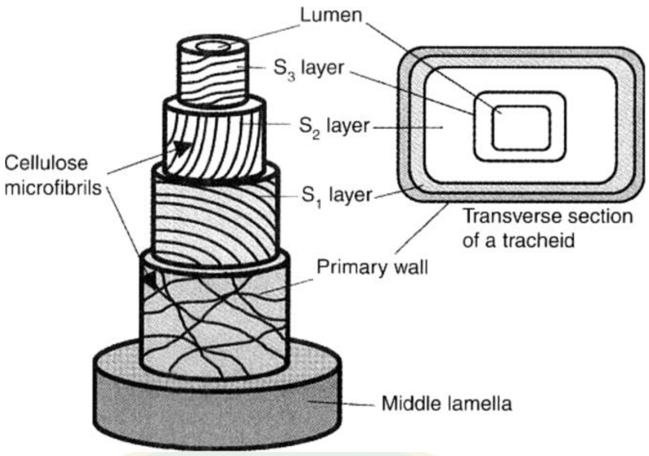

Figure 11 Three dimensional sketch of a tracheid (xylem cell), copyrighted by the American society of plant biologists and reprinted with permission.

The main lignocellulosic waste streams from industries originate from the pulp and paper industry. Example of these streams are waste paper products, fiber waste, sulphite liquor, sludge, and other solids from the pulp and paper mills. Moreover, a large part of the municipal solid waste is food waste, where lignocelluloses can be found in peels, stems, and leaves, etc. from fruits, flowers, and vegetables. A study in the U.S. found that the lignocellulosic content of food waste was 55.4% cellulose, 7.2% hemicelluloses, and 11.4% lignin (Barlaz, 2006).

Pretreatment to improve the digestibility of lignocellulosic biomass

The properties of lignocellulosic biomass render it resistant to biodegradation. Due to the complexity and variability of biomass chemical structures, the optimal pretreatment method and conditions depend on the types of lignocellulose present. Several structural and compositional properties were found to have impacts on the biodegradability of lignocellulosic biomass, including cellulose crystallinity, accessible surface area, degree of cellulose polymerization, presence of lignin and hemicellulose, and degree of hemicellulose acetylation (Zheng, 2014). The goal of pretreatment is to alter such properties to improve biomass amenity to enzymes and microbes.

These pretreatment methods can be divided into mechanical, thermal, chemical as well as, biological treatments or a combination of these techniques as it is shown in Table 11. Co-digestion is yet another method used to enhance biogas production. This method entails planning loading of the digester so that an advantageous blend of different substrates serve as organic load. The effects of different pretreatment techniques on the chemical composition and physical characteristics of lignocellulosic biomass are summarized in Table 12 (Hendriks, 2009).

Table 11 A summary of techniques investigated for enhancing biogas production from lignocellulosic materials.

Technique	Subdivision
Mechanical	Milling
Thermal	Steam explosion Thermal hydrolysis
Chemical	Acid hydrolysis Alkaline pretreatment Ionic liquids pretreatment Oxidative pretreatment
Biological	Fungi
Co-digestion	Two or more substrates

Table 12 Effect of pretreatment on the compositional and structural alteration of lignocellulosic biomass.

Pretreatment	Increase of accessible surface area	Decrystallization of cellulose	Solubilization of hemicellulose	Solubilization of lignin	Alteration of lignin structure
Mechanical	●	●			
Irradiation	●	○	○		
Steam-explosion	●		●	○	●

Liquid hot water	●	ND	●	○	○
Catalyzed steam-explosion	●		●	●/○	●/○
Alkaline	●		○	●/○	●
Oxidative	●	ND		●/○	●
Ionic liquids	●	●	○		
Thermal acid	●	ND	●		
Thermal alkaline	●	ND	○	●/○	●
Thermal oxidative	●	ND	○	●/○	●

a● = major effect, ○ = minor effect, ND = not determined, and blank = no effect.

The effects of the aforementioned lignocellulosic biomass properties on enzymatic hydrolysis for bioethanol production were comprehensively reviewed by Zheng (2009), but only a few studies have reported on the correlation between biogas production and lignocellulosic biomass properties, with most focusing on cellulose crystallinity and lignin content. One exception is a study by Akhand andMéndez Blancas (2012) on the relationship between biogas yield and surface area of the substrate. It revealed that increased accessible surface area of wheat straw enhanced methane yield.

Physical pretreatment

Physical pretreatment refers to methods that do not use chemicals or microorganisms during the pretreatment processes. Previously developed physical pretreatment techniques include comminution, steam-explosion, liquid hot water pretreatment, extrusion, and irradiation (Zheng et al., 2014).

Chemical pretreatment

For this paper, chemical pretreatment refers to the use of chemicals, such as acids, bases, and ionic liquids, to alter the physical and chemical characteristics of lignocellulosic biomass. Among the three pretreatment categories discussed, chemical pretreatment has received the most research interest. Although many chemical pretreatment methods have been studied for cellulosic ethanol production, only some of them have been applied to biogas production in AD processes (Zheng et al., 2014).

Biological pretreatment

Biological pretreatment for enhancement of biogas production in anaerobic digestion has mainly focused on fungal pretreatment, pretreatment by microbial consortium, and enzymatic pretreatment. Ensiling has also been studied as a pretreatment for biogas production. However, long pretreatment time has limited the use of these processes in commercial application (Taherzadeh and Karimi, 2008). In addition, there is competition for carbohydrates between pretreatment and downstream biogas production, because certain levels of carbohydrates are required by microbes during biological pretreatment. On the other hand, the accessibility of cellulose is increased after pretreatment, which can improve biogas production. Therefore, one major objective of biological pretreatment is to minimize the loss of carbohydrates and maximize the lignin removal for AD feedstocks with high digestibility (Zheng et al., 2014).

Combined pretreatment

Lignocellulosic biomass pretreatment by physical, chemical, or biological means has been extensively investigated for enhancing biogas production in AD process. Since biodegradability of biomass is limited by several factors such as crystallinity of cellulose, lignin content, and interlinkages between hemicellulose and lignin, a single pretreatment method does not provide efficient results due to its limited specific functioning mode (e.g. NaOH primarily targets lignin, but not hemicellulose) and intrinsic disadvantages. Therefore, no one pretreatment method (physical, chemical, or biological) can be declared a “winner”. Combined pretreatment incorporating two or more pretreatment techniques from the same or different categories are also common. A combination of alkali with ultrasound was employed to treat rice stalks, resulting in 35-48% higher daily biogas production than the pretreatment, which used only an alkali, and 67-77% higher than no treatment (Wang et al., 2012). With this combined pretreatment, 41% lignin in the stalks was degraded. Nkemka andMurto (2013) demonstrated that a combination of acid catalyzed steam treatment with enzymatic hydrolysis of wheat straw improved methane yield by 57% compared to untreated wheat straw. Michalska andLedakowicz (2013) also reported that a combination of NaOH treatment with enzymatic hydrolysis of *Sorghum Moench* resulted in 300% and 50% higher methane yield than NaOH and enzymatic treatment alone, respectively. Compared with single pretreatment methods, combined pretreatment could be beneficial due to higher methane yield, reduced pretreatment severity, and more complete biomass utilization; however, it may also increase pretreatment costs, thus an economic analysis is needed to determine biogas energy production costs for combined biomass pretreatment methods.

Solar heated biogas system

The solar water heating system using evacuated tubes with auxiliary electrical heater was adopted to charge the thermal energy to the bioreactor, which made the bioreactor work regularly (Dai et al., 2008). A low-cost solar water heating system was installed to enhance the biogas production in the digester under mesophilic process conditions (Ali and Al-Sa’ed, 2018). A solar hot water system in the digester was used to increase the process temperature and enhance the anaerobic microorganisms during the cold winter season. The pilot scale digester (Figure 12) consisted of fermentation tank (main digester) which was connected to other components including: mixing tank, hot water solar system, biogas storage balloon, and solid waste collective tub (digested slurry). Both mixing and fermentation tanks (digester), cylindrical in form, are constructed of high-quality plastic materials and internal capacity to working volume. The anaerobic digester volume was calculated based on the organic loading rate (OLR) to accommodate the daily amount of manure produced by the farm.

Figure 12 Solar heated biogas system (Koçar and Eryaşar, 2007).

Technological aspects of biogas purification

Biogas can be used in the engines of transport vehicles and blended into natural gas networks, but it also requires the removal of carbon dioxide, hydrogen sulphide, and moisture. Biogas purification process flow diagrams have been developed for a process enabling the use of a dolomite suspension, as well as for solutions obtained by the filtration of the suspension, to obtain biogas free of hydrogen sulphide and with a carbon dioxide content that does not exceed 2%. The cost of biogas purification was evaluated on the basis of data on biogas production capacity and biogas production cost obtained from local water treatment facilities. It has been found that, with the use of dolomite suspension, the cost of biogas purification is approximately six times lower than that in the case of using a chemical sorbent such as monoethanolamine. The results showed travelling costs using biogas purified by dolomite suspension are nearly 1.5 time lower than travelling costs using gasoline and slightly lower than travelling costs using mineral diesel fuel.

The methanation is a technology for processing organic waste and green energy generation. It consists in the transformation of the organic matter present in the waste into biogas. The quality of biogas (it is mixture of gases) is an important character for his energetic and economic valorization since it depends on the content of gases constituent primarily methane, carbon dioxide and hydrogen sulfide. Generally, the compound biogas from about 55 to 70 % of CH_4, 30-45 % of CO_2, and traces of NH_3 (80-100 ppm), H_2O (1000-3000 ppm) and hydrocarbons (<100 ppm). The CH_4 has an energetic interest because it has a high calorific value of the order 9.94 kWh/m^3. As against the CO_2 is a gas without energetic interest and his presence in the biogas in large quantities which can reduce its energetic value. The H_2S is a corrosive element for metals constitutes motors cogeneration consequently it may destroy them and corrode pipes of station for methanation (Elasri et al., 2015).

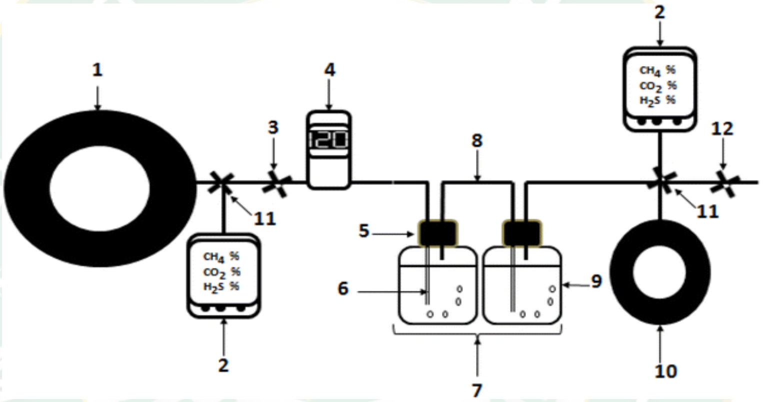

Figure 13 Experimental device of purification test. 1 Inner tube of raw biogas, 2 Biogas analyzer, 3 Valve for flow control, 4 Digital flow meter, 5 Silicone plug, 6 Pastor pipette, 7 Filtration system, 8 Silicone tube, 9 Bottle, 10 Inner tube of purified biogas, 11 Valve of three-lane, 12 Valve of two-lane (Elasri et al., 2015).

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Therefore, a good economic and energy quality of biogas when it contains a high content of methane and must be without CO_2 and H_2S. Actually, the production of biogas from methanation unit needs a passage in a purification phase for the removal of these harmful gases. So, the purification of biogas has become a requirement to obtain a good biogas quality with a high calorific value and without of corrosive impurities in Figure 13 (Elasri et al., 2015).

Biogas purification and upgrading had been researched extensively in recent years. (Hosseini and Wahid 2010) reviewed biogas purification processes with the focus on contaminants removal, while (Ryckebosch et al., 2012) reported on various techniques for biogas transformation regarding their conditions, functioning, bottlenecks and efficiency. (Bauer et al., 2004) reviewed the commercial technologies on biogas upgrading. Most recently, (Munoz et al., 2006) provided a state of the art review on the biogas upgrading technologies with emphasis on biotechnologies for CO_2, H_2S, Siloxanes and halocarbon removal. (Sun et al., 1978) worked on appropriate biogas upgrading technology, focusing on product purity and impurities, methane recovery and loss, upgrading efficiency, investment and operating cost. From the literature, the main techniques for biogas upgrading and purification are: water scrubbing, adsorption (physical and chemical), cryogenic separation, membrane technology, biological upgrading and in-situ upgrading methods.

CO_2 Removal from gas stream

Removal of CO_2 is necessary in order to increase the density and calorific value of the gas to meet Wobbe Index quality and specifications. The current technologies are: pressure swing adsorption, physical absorption (water and organic solvent scrubbing), chemical absorption, cryogenic separation, membrane separation, biological methane enrichment. These are discussed in the order of old, current trends, and future technologies and ideas.

Related research

Water hyacinth and sheep waste can be used to generate energy which could save on the fossil fuels conventionally used as source of energy. In this study, the possibility was explored to mix water hyacinth with sheep waste in different combinations for anaerobic co-digestion, so that energy can be generated as biogas and at the same time digested sludge can be used as fertilizer for agricultural applications. Pretreatment of water hyacinth was done by alkali method. Anaerobic co-digestion was carried out in mesophilic temperature range of 30-37°C with different fermentation slurries of 8% total solids. Co-digestion was carried for a retention period of 60 days. The gas produced was collected by the downward displacement of water, and was subsequently measured and analyzed. Fermentation slurry sheep waste 3 (mixing ratio of 4: 12.01:83.90 for Water Hyacinth: Sheep Waste: Water) was found to be optimum, which gave the highest biogas yield of 0.36 l/gVS. With composition 60.84% % CH_4, 21.53% CO_2 and 17.63% others (H_2, N_2, H_20 and H_2S). The overall results showed that blending water hyacinth with Sheep waste had significant improvement on the biogas yield. (Patil et al., 2014)

Biogas or CH_4 is traditionally produced via anaerobic digestion, or recently by thermochemical or a combination of thermochemical and biological processes via syngas (CO and H_2) fermentation. However, many of the feedstocks have recalcitrant structure and are difficult to digest (e.g., lignocelluloses or keratins), or they have toxic compounds (such as fruit flavors or high ammonia content), or not digestible at all (e.g., plastics). To overcome these challenges, innovative strategies for enhanced and economically favorable biogas production were proposed in this review. The strategies considered are commonly known physical pretreatment, rapid decompression, autohydrolysis, acid or alkali pretreatments, solvents (e.g. for lignin or cellulose) pretreatments or leaching, supercritical, oxidative or biological pretreatments, as well as combined gasification and fermentation, integrated biogas production and pretreatment, innovative biogas digester design, co-digestion, and bio-augmentation. (Patinvoh et al., 2017)

Liquid hot water and alkaline pretreatments of giant reed biomass were compared in terms of digestibility, methane production, and cost-benefit efficiency for electricity generation via anaerobic digestion with a combined heat and power system. Compared to Liquid hot water pretreatment, alkaline pretreatment retained more of the dry matter in giant reed biomass solids due to less severe conditions. Under their optimal conditions, Liquid hot water pretreatment (190°C, 15 min) and alkaline pretreatment (20 g/L of NaOH, 24 h) improved glucose yield from giant reed by more than 2-fold, while only the alkaline pretreatment significantly ($p < 0.05$) increased cumulative methane yield (by 63%) over that of untreated biomass (217 L/kg VS). Liquid hot water pretreatment obtained negative net electrical energy production due to high energy input. Alkaline pretreatment achieved 27% higher net electrical energy production than that of non-pretreatment (3859 kJ/kg initial total solids), but alkaline liquor reuse is needed for improved net benefit. (Jiang et al., 2016)

Palm kernel cake mainly composed of mannan, lignin and protein, is abundant renewable resourcewith commercial value. To develop clean and efficient way for Palm kernel cake refinery, the method based on the synergism of hot water pretreatment, steam pretreatment and enzymatic hydrolysiswere developed. Hot water pretreatment of 180°C, 20 min and steam pretreatment of 121°C, 20 min showed similar performance for sugarrelease from Palm kernel cake. The main saccharides produced from PKC by hot water pretreatment and steam pretreatment were mannose and manno-oligosaccharides, while no furfural formed. The surface structure analyzed by SEM showed that hot water pretreatment enhanced the microporosity of Palm kernel cake and the accessibility of which was increased thereafter. When hot water pretreatment pretreated Palm kernel cake was further hydrolyzed with enzyme cocktail (cellulase, xylanase, endo-mannanase), 45% of Palm kernel cake was solubilized compared with the control. The manno-oligosaccharides produced by hot water pretreatment and steam pretreatment were converted to mannose and mannobiose by endo-mannanase. The results suggested that both hot water pretreatment and steam pretreatment promote enzymatic hydrolysis of Palm kernel cake by releasing oligosaccharides and enhancing microporosity, and the synergism of which was effective for Palm kernel cake decomposition. (Mi et al., 2016)

CHAPTER 3
MATERIAL AND METHODS

This study was conducted to determine the optimal and efficient pre-treatment condition for enhanced biogas production. The sample was collected from longan garden and was subjected to pretreatment and fermentation processes to produce biogas (Figure 14).

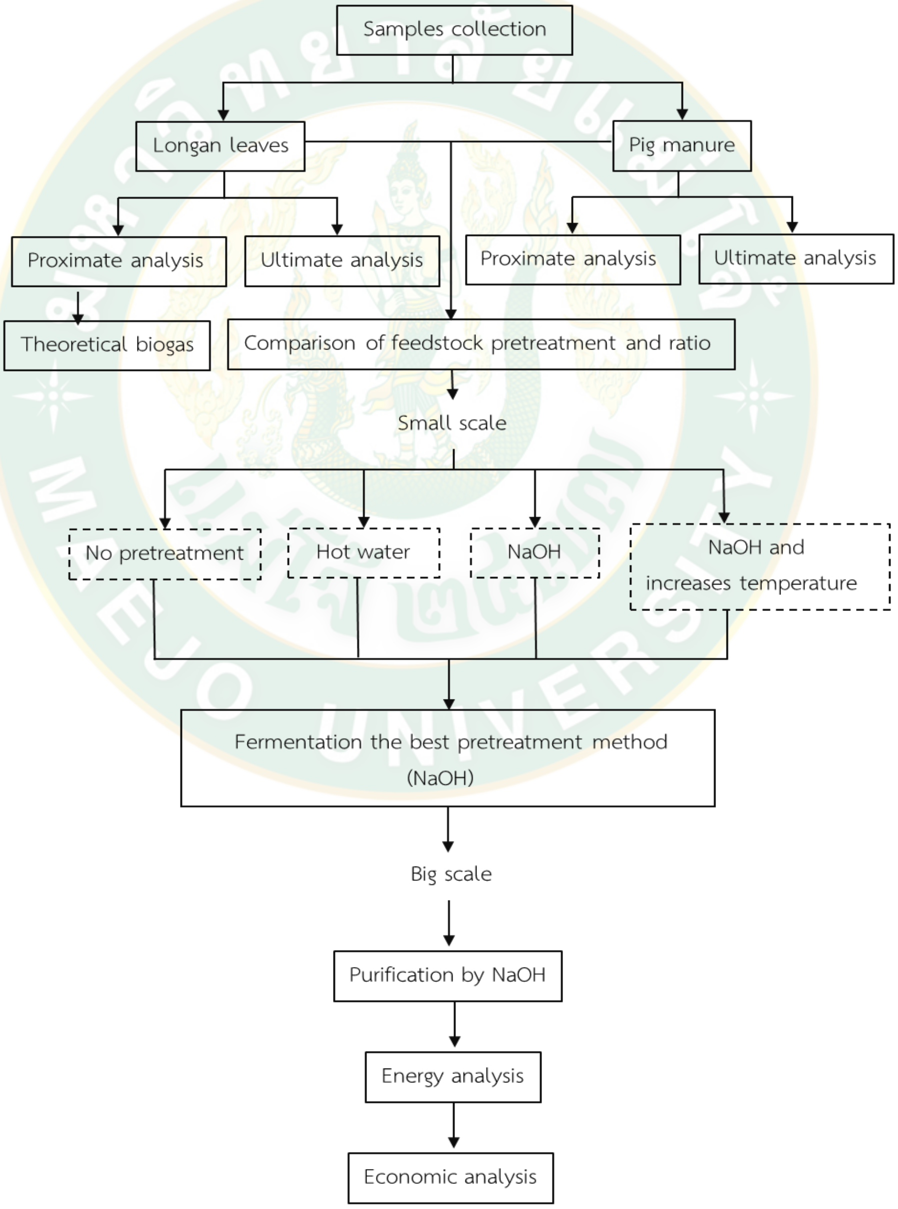

Figure 14 The flow process of biogas production by co-digestion used on this study.

Experiment 1. Material collection and preparation

Longan leaves were obtained at Sansai, Chang Mai, Thailand. The leaves was crushed into small pieces by a grinding machine. Pig manure was collected from swine farm at the Faculty of Animal Science and Technology Maejo University, Chang Mai, Thailand. The collected samples were transferred to the lab of Energy Research Center, Maejo University as shown in Figure 15.

Figure 15 Material collection and preparation. (a) Longan leaves collection, (b) Separation of leaves and stalk, (c) small particles, and (d) pig manure.

Experiment 2. Potential of biogas production from longan leaves

Materials preparation for biomass analysis

Preparation of the leaves were shown in Figure 16. The pre-processed longan leaves were dried in an oven for 48 h at 40°C to achieve a moisture content of less than 10% andwas then grinded using a blender (OTTO BE-127 blender). The dried powder was stored and sealed in a desiccator under ambient temperature for further usage. The experiment was carried out in the Energy Research Center, Maejo University, Chaing Mai, Thailand. For all experiments, longan leaves were used for preliminary laboratory analysis to estimate biogas potential.

Figure 16 Material Preparation. (a) Dried longan leaves (b) Powdered longan leaves (c) pig manure.

Analytical methods

The samples were analyzed for total solids (TS), volatile solids (VS), chemical oxygen demand (COD) (Federation and Association, 2005) and pH by standard methods. Elemental composition (C, H, N, O, and S) was analyzed using the element analyzer Perkin-Elmer.

Moisture content of raw materials was determined following the procedure given in ASTM Standard D 4442-07. About one (1) gram of the sample was taken in to a crucible and oven-dried for one (1) hour at 105±5°C and until constant weight was obtained.

$$\text{Moisture content (\%wd)} = \frac{w2-w3}{w2-w1} \times 100 \qquad \text{Eq. 1}$$

Where, w_1 = weight of crucible, g w_2 = weight of crucible + sample, g w_3 = weight of crucible + sample after heating.

The residual sample in the crucible was heated without lid in a muffle furnace at 700±50°C for one and a half hour. The crucible was then taken out, cooled and desiccated and weighed until contant weight was obtained. The residue was reported as ash on percentage basis.

$$\text{Ash content (\%wd)} = \frac{w3-w1}{w2-w1} \times 100 \qquad \text{Eq. 2}$$

Where, w_1 = weight of the empty crucible, g w_2 = weight of empty crucible + sample, g w_3 = weight of the crucible + ash, g Ash.

Determination of volatile matter: The dried sample left in the crucible was covered with a lid and placed in a muffle furnace, maintained at 925±20°C for 7 minutes. The crucible was cooled,desiccated and weighed again. Loss in weight was reported as volatile matter on percentage basis.

$$\text{Volatile matter (\%wd)} = \frac{w2-w3}{w2-w1} \times 100 \qquad \text{Eq. 3}$$

Where, w_1 = weight of the empty crucible, g w_2 = weight of empty crucible + sample, g w_3 = weight of the crucible + sample after heating.

The fixed carbon in percentage was calculated by difference between 100 and the sum of the volatile matter, moisture and ash content.

$$\text{\%fixed carbon (\%wd)} = 100 - (\text{moisture content} + \text{volatile matter} + \text{ash}) \qquad \text{Eq. 4}$$

Theoretical biogas estimation

Biogas is a product of breaking down organic matter, such as proteins, lipids, and carbohydrates, through anaerobic digestion using anaerobic bacteria. When the chemical composition of a substrate (C, H, O, N and S) is known, it can be predicted from the stoichiometric formula developed by (Buswell and Boruff, 1932).

Biogas potential production was calculated according to Von Sperling and Chernicharo (Von Sperling and de Lemos Chernicharo, 2005). Theoretical methane potential was calculated from Bushwell's formula (eq. 5) which is derived by stoichiometric conversion of the compound to methane (CH_4), carbon dioxide (CO_2) and ammonia (NH_3) (Gilcreas, 1966).

$$C_aH_bO_cN_d + \left(\frac{4a-b-2c+3d}{4}\right)H_20 \rightarrow \left(\frac{4a+b-2c-3d}{8}\right)CH_4 + \left(\frac{4a-b+2c+3d}{8}\right)C0_2 + dNH_3\text{-} \qquad \text{Eq. 5}$$

Experiment 3. Efficiency of pretreatment on longan leaves for biogas production co-digestion with pig manure

Response surface methodology (RSM)

The design of experiment (DOE) is a fundamental statistical tool for engineering field (Witek-Krowiak et al., 2014). DOE refers to the process of planning, designing and analyzing the experiment data so that valid and object conclusions can be concluded effectively and efficiently (Aagaard et al., 2014). This improves the process by considering only most significant factors, and also cost-effective and time efficient (Skinner et al., 2002). Design Expert software to develop mathematical models that relate the process input parameters to the output features as responses. The RSM approach was used to conduct the optimization of all experimental work in this study. The two main factors of AD process considered are ratio and time. The output features investigated are production of biogas compositions.

Pretreatment of longan leaves

In this study, three (3) different pre-treatment processes were conducted:

- Pretreatment of longan leaves by 2% NaOH for 72 h.
- Pretreatment of longan leaves by hot water 100°C for 2 h.
- Pretreatment of longan leaves by 2% NaOH and kept at solar dryer at 60°C for 72 h.

The pretreated longan leaves morphological isolates was examined under the scanning electron microscope to determine its efficiency in the production of biogas by co-digestion with pig manure.

SEM sample preparation

The longan leaves were examined under Scanning Electron Microscope (SEM) for determination of the morphology of the isolates. The samples were cut into suitable sizes around 1 cm and dipped into -20°C liquid nitrogen and dried. The dried samples were then sputter-coated with and fixed with the brass stub for examination under the FESEM (Field Emission Scanning Electron Microscope) (Nova Nanosem 450, USA). Instrument used: JSM-5410LV operates with a field emission gun and observations were performed at a total magnification of 1000X.

Figure 17 Scanning electron microscopy (SEM).

Effect of pretreatments longan leaves for biogas production by co-digestion with pig manure

Experimental design for co-digestion

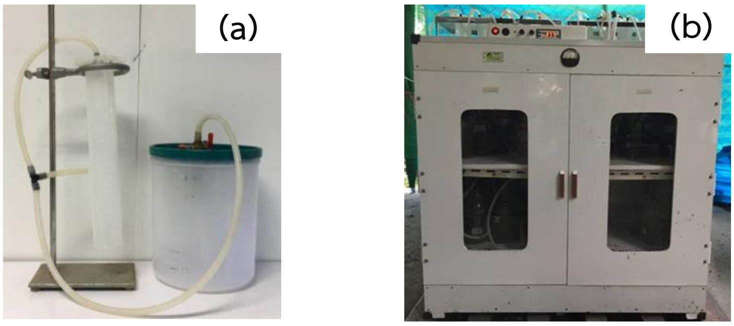

Figure 18 (a) Water tank 6 L by connecting with cylinder 1,000 ml (b) Biogas production under controlled temperature condition.

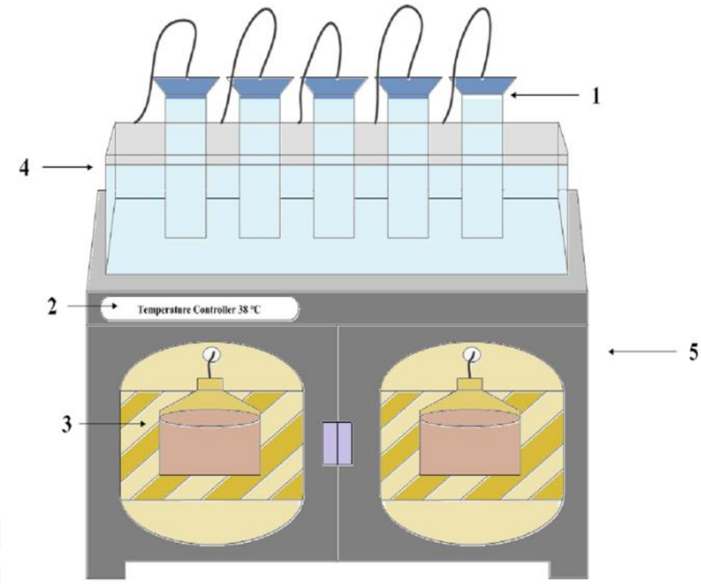

Figure 19 Schematic view of the experimental set up during anaerobic digestion of teak leaves. 1) Gas measuring cylinder, 2) temperature controller, 3) digester, 4) Water bath 5) incubator box.

The experiment produces biogas by batch system using lab-scale digesters fabricated from 6 L water tank by connecting with cylinder 1,000 ml to gas collection, gas measuring and a feed inlet. It was sealed using a rubber stopper with a pipe to extract biogas as shown in Figure 18. Experiment was divided into three (3) treatments:(T1) biogas production by co-digestion of pig manure with longan leaves pretreated with 2% NaOH for 72 h; (T2) biogas production by co-digestion of pig manure with longan leaves pretreated with hot water at 100°C for 2 h; (T3) biogas production by co-digestion of animal manure with longan leaves pretreated by 2%NaOH and solar dryer at 60°C for 72 h. , with a ratio of 5 longan leaves : 5 pig manure (280 g : 668 g),d controlled pH 7.2-7.8, and total solids (TS) at 10%. Experiment was conducted simultaneously under mesophilic temperature at 37°C for 45 days. Each digester was manually mixed twice a day. Shown in (Figure 18 and 19).

Analytical methods

The solid contents, including total solids (TS) and volatile solids (VS) were characterized using the Standard Methods for the Examination of Water and Wastewater (Federation and Association, 2005). When testing SCOD (soluble chemical oxygen demand), samples were initially centrifuged at 10,000 rpm for 5 min and determined by spectrophotometric method (Federation and Association, 2005). The pH of the sample were adjusted to 4.3 using the $CaCO_3$ and titrated against sulfuric acid following the method by Snoeyink and Jenkins, 1980. Total fat, ash, moisture, fiber contents and volatile fatty acids (VFA) were determined using AOAC official method (Apha, 1995) while the pH value was tested by a pH meter (B-711, Horiba, Japan)and the composition of biogas (CH_4, CO_2 and O_2) was measured using a biogas analyzer (BIOGAS 5000, Geotech).

Experiment 4. Enhanced biogas production efficiency of longan leaves co-digestion with pig manure by solar heating

The experimental design 200 L biogas production system

Figure 20 200 L biogas digester system.

The experiment produces biogas by batch system using digesters fabricated from 200 L water tank by connecting with biogas storage tank 120 L and solar collector system shown in Figure 20 and 21. The component of biogas digester include agitator which works by using a motor and heat exchanger which has a diameter of 2 cm and length 170 cm and works by using a water pump). Experiment 4 is the determination of effcient pre-treatment method of longan leaves. The three different treatments were subjected to co-digestion with pig manure at controlled mesophillic temperature (37°C). The samples with various parameters were analyzed every 7 days using standard methods shown in experiment 3.

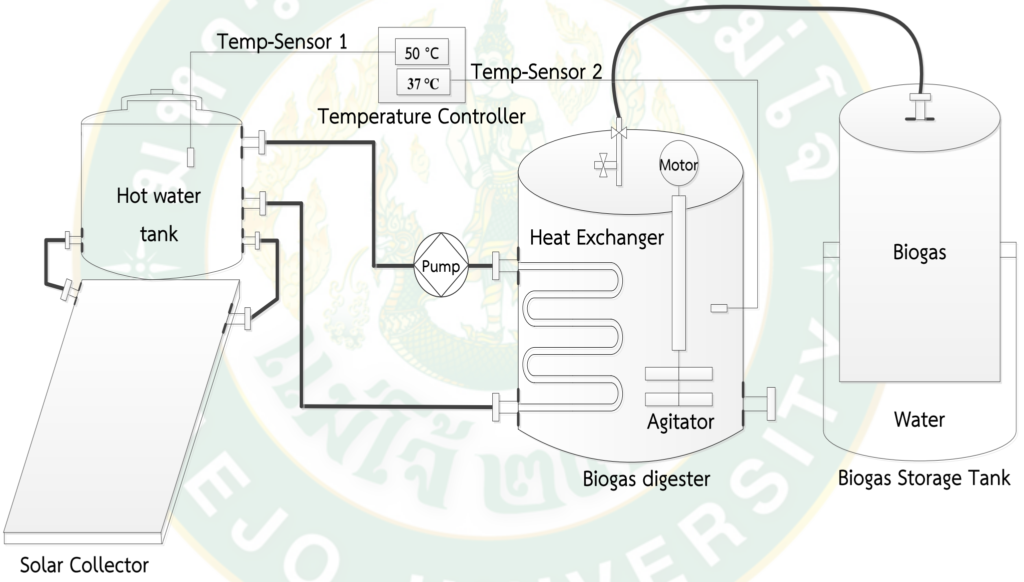

Figure 21 The component of enhanced biogas production efficiency by solar energy.

Solar collector system

In thermosiphon sytem, the water is heated and the fluid will be circulated naturally without the use of mechanical pump. The heat transfer increases the temperature and is most efficient in areas with high levels of solar radiation.

Figure 22 Solar collector system.

System of enhanced biogas production efficiency by solar collector

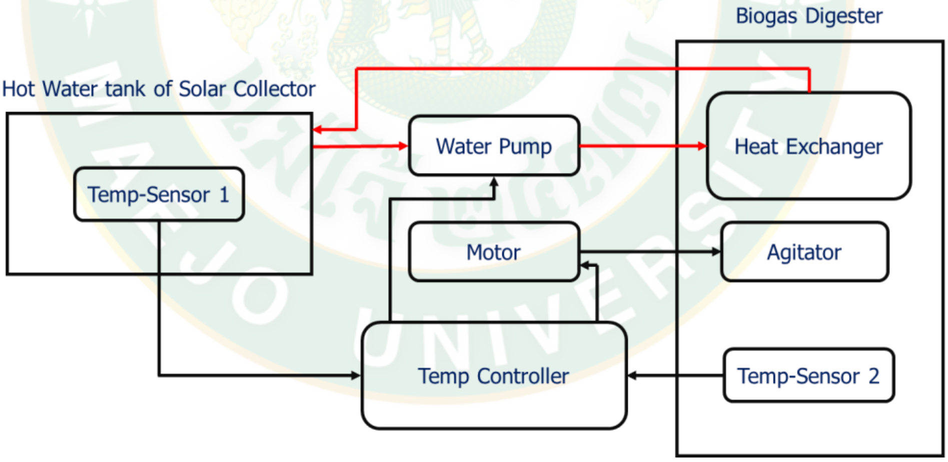

Figure 23 Diagram of enhanced biogas production efficiency by solar energy.

Operation of the automatic enhanced biogas production by solar collector system. The system include two (2) temperature sensor, temperature sensor I wasinstalled at the outlet of hot water tang of solar collector to monitor the water temperature while the temperature sensor II was installed inside biogas digester to check temperature inside the biogas digester. When water temperature increases to

50°C, temperature sensor I will send a signal to a controller for to start water pump and motor. Hot water will flow inside the biogas digester and return hot water back to hot water tang and the motor will start working. For the system to continue working, the temperature in the water tank must be maintained and not go beyond 40°C and the temperature inside the biogas digester should be 37°C or lower. The component of enhanced biogas production efficiency by solar energy was shown in Figure 20 and diagram of enhanced biogas production efficiency by solar energy was shown in Figure 23.

Experiment 5. Biogas purification by sodium hydroxide

In this study, the obtained biogas from fermenter is continually purified by sodium hydroxide solution at different concentrations (1, 2, and 3%) for 20 min and the flow rate wa set up at 7.6 L/min (Yincheng et al., 2011). The percentage of components of the output biogas were tested every 5 min by gas checker (BIOGAS 5000, Geotech). Figure 24 shows the biogas purification system.

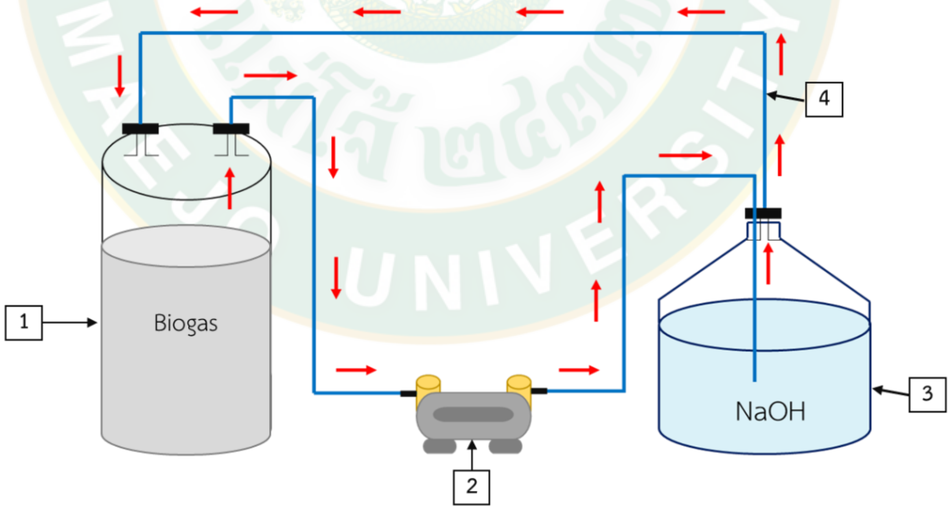

Figure 24 Biogas purification system through sodium hydroxide 1) biogas storage container 2) air pump 3) sodium hydroxide storage tang 4) Biogas pumping direction.

Energy content analysis

Calorific values were estimated according to Chuanchai and Ramaraj, 2018. The higher calorific values (HCV) and lower calorific values (LCV) of pure methane was 39.82 and 35.87 MJ/m^3, respectively. HCV and LCV of produced biogas were determined according to the following formula:

$$HCVbiogas = 0.3989 \times MC = 0.0213 \ (R2 = 1) \qquad \text{Eq. 6}$$

$$LCVbiogas = 0.3593 \times MC = 0.0192 \ (R2 = 1) \qquad \text{Eq. 7}$$

Where; MC is the methane content in biogas (%).

Experiment 6. Digestate fertilizer analysis

The samples were analyzed for organic carbon, nitrogen (alkaline $KMnO_4$ method), 0.5 M $NaHCO_3$ (pH 8.5) extractable P and 1 N NH_4OAc- extractable K and other trace elements (Page Jr and Laidlaw Jr, 1982). In addition, Emission, atomic absorption, volumetric, colorimetric, and photometric methods were used to determine physicochemical digestate properties measurements were adopted from Castro et al., 2017

Experiment 7. Economic analysis

Energy demand is continuously rising because of increase in population and industrial development. Currently there is huge difference in consumption and availability of energy resources. Energy shortage in developing countries is one of the major challenges for sustainable development. Such challenges can be met and managed via indigenous, clean and reliable alternate energy sources like biogas and bioenergy especially at household levels. Biogas is a methane rich gas that is being generated by anaerobic fermentation of organic material and a biogas plant can effectively utilize various feedstock sources including animal manure, vegetable-fruit waste, sugar, poultry waste and molasses etc. Research (Yasar et al., 2017) the results shown that 1 kW of energy can be generated from 0.65 m^3 of biogas by such household biogas units, furthermore it was evident that fixed dome type biogas plants were more economical with shortest payback period of about four months. Additionally effluent slurry being generated by such biogas plant can be a profitable provision in-terms of bio-fertilizer for agricultural.

In this work, a scale-up biogas production from longan leaves co-digestion with pig manure (200 L) was used for evaluation. All of the materials used in this test was collected on the year of 2018. Biogas and bioenergy technologies have been proven the environmentally safer with fewer or lowest health impacts, economically effective and helpful in energy conservation.

CHAPTER 4
RESULTS AND DISCUSSION

Physico-chemical properties of longan leaves

The physico-chemical characterizations of longan leaves were done and shown in Table 13. Results showed 6.52 moisture, 16.52 ash, 76.82 volatile matter and 6.11 fixed carbon comprises the longan leaves.

Table 13 Physical, chemical and composition of longan leaves.

Parameters	longan leaves
Proximate analysis	
- Moisture	9.61
- Ash	7.46
- Volatile matter	76.82
- Fixed carbon	6.11
Ultimate analysis	
- Carbon (%)	47.33
- Hydrogen (%)	5.69
- Oxygen (%)	40.48
- Nitrogen (%)	5.67
- Sulphur (%)	0.23
Composition and others	
- pH	4.86
- TS (mg/kg)	892,473
- VS (mg/kg)	833,384
- COD (mg/g)	114,000

The total solids (TS) and volatile solids (VS) content of the sample were 892,473 mg/kg and 833,384 mg/kg, respectively. The average pH was 4.86 and the recorded average COD was 114,000 mg/g. The best pH values of biogas production ranged from

7 to 8 and a total solid (TS) content of 8% (Zhang et al., 2013). The process is severely inhibited if the pH decreases below 6.0 and rises above 8.5 in which too much total solid will be difficult to biodegrade (Dussadee et al., 2017).

Theoretical analysis of longan leaves biogas and biochemical methane production

Biogas is a product of breaking down of organic matter, such as proteins, lipids, and carbohydrates through anaerobic digestion using anaerobic bacteria. When the chemical composition of a substrate (C, H, O, N and S) is known, it can be predicted from the stoichiometric formula developed by (Buswell and Boruff, 1932). The calculation process wass shown in equation 5, which was used to calculate the amount of methane and carbon dioxide. The calculation for the elemental composition of substrate was shown in Table 14. The biogas content were calculated and found to have 43.66% methane, 47.03% carbon dioxide, and 9.31% ammonia as shown in Table 15. The longan leaves contained different chemical composition such as carbon, hydrogen, oxygen, nitrogen and sulphur for about 47.33%, 5.69%, 40.48%, 5.67% and 0.23% respectively.

$$\mathrm{C_aH_bO_cN_d} + \left(\frac{4a-b-2c+3d}{4}\right)\mathrm{H_2O} \rightarrow \left(\frac{4a+b-2c-3d}{8}\right)\mathrm{CH_4} + \left(\frac{4a-b+2c+3d}{8}\right)\mathrm{CO_2} + \mathrm{dNH_3}\text{-}$$

Several studies have been conducted in the physical, chemical and composition of longan leaves which gave appropriate ways to estimate the theoretical biogas production of the longan leaves to compare the bioavailability of the sampled leaves to other plant leaves. The theoretical biogas composition, total biogas production and total theoretical amount of gas of different plant leaves were presented in Figure 25 and Table 16.

Table 14 Proximate and ultimate analysis of leaves.

Parameters Plant leaves Material	Proximate analysis (%)		Ultimate analysis (%)						Reference
	M	A	C	H	O	N	S	HHV (MJ/kg)	
Semi dried banana	8.3	8.7	43.5	6.3	48.7	1.3	0.2	19.8	(Jena et al., 2017)
Wet banana	74.7	12.2	15.9	9.2	73.4	1.4	0.05	5.5	
Elephant grass	12.2	4.9	41.2	5.5	46.6	1.8	-	14.7	(Sellin et al., 2016)
Wheat	4.60	4.9	44.9	5.71	43.8	0.63	-	17.3	
Sena	-	17.30	36.20	4.72	37.49	4.29	-	18.13	(Shen et al., 2010)
Almond tree	-	-	43.25	5.50	48.06	2.85	0.34	17.6	(García et al., 2014)
Apple tree	-	-	44.45	6.15	47.56	1.61	0.23	17.5	
Cherry tree	-	-	45.52	6.25	46.55	1.49	0.19	17.7	
Chestnut	-	-	47.82	6.24	43.46	2.21	0.27	18.8	
Feijoa	-	-	45.28	6.03	47.25	1.23	0.20	17.8	
Hazelnut tree	-	-	45.14	6.79	45.71	2.05	0.31	17.8	
Oak tree	-	-	46.90	5.47	44.20	3.04	0.38	18.3	
Orange tree	-	-	41.11	5.28	50.62	2.59	0.40	16.2	
Palm	9.00	12.32	40.40	5.58	52.09	1.94	-	-	(Abnisa et al., 2013)
Cardoon	-	29.60	34.10	4.90	29.80	1.40	0.20	17.90	(Damartzis et al., 2011)
Bamboo	-	11.00	40.50	5.80	52.80	0.70	0.20	-	(Huang et al., 2011)
Longan	6.52	16.52	47.33	5.69	40.48	5.67	0.23	-	This study

Table 15 Biogas composition and production of longan leaves.

Biogas Composition (%)	Yield
CH_4	43.66
CO_2	47.03
NH_3	9.31
Biogas Production (m^3/kg)	
CH_4	0.4263
CO_2	0.4589
NH_3	0.0914
Biogas	0.9766

Note: Calculation examples as Appendix A

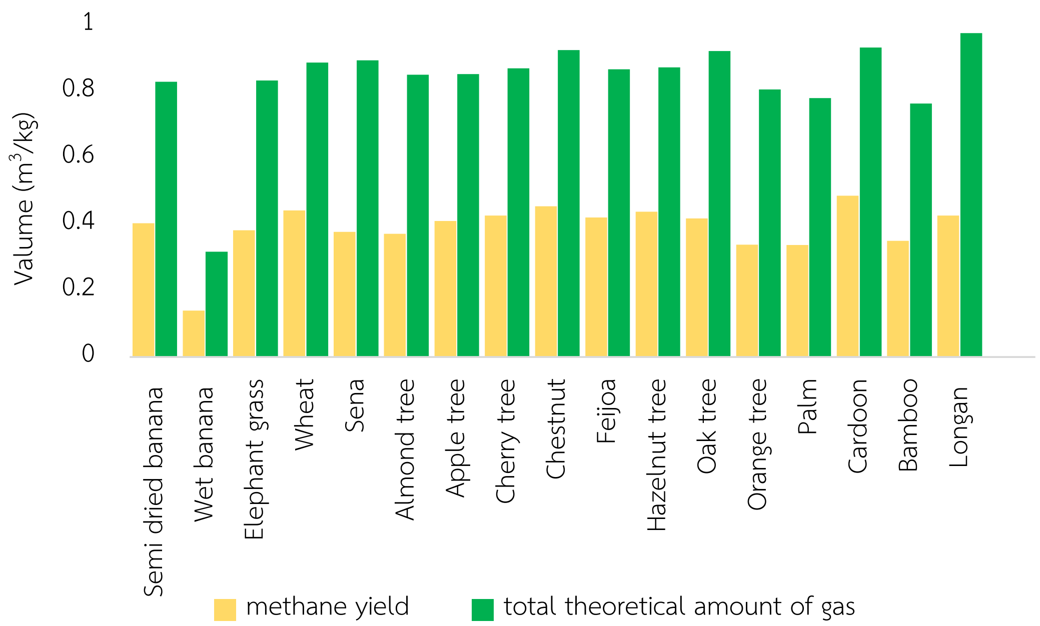

Figure 25 Potential production of methane and total biogas from different plant leaves material.

Table 16 Biogas composition, total biogas production and theoretical biogas yield of different plant leaves.

Parameter Plant leaves Material	Gas composition (%)			Total gas production (m^3)			Total theoretical amount of gas m^3/Kg
	CH_4	CO_2	NH_3	CH_4	CO_2	NH_3	
Semi dried banana	48.53	48.97	2.50	0.4034	0.4060	0.0206	0.8300
Wet banana	44.08	48.90	7.02	0.1403	0.1553	0.0221	0.3177
Elephant grass	45.70	50.69	3.61	0.3820	0.4225	0.0299	0.8344
Wheat	49.74	49.08	1.19	0.4422	0.4352	0.0105	0.8878
Sena	42.06	48.72	9.22	0.3774	0.4357	0.0819	0.8951
Almond tree	43.66	51.00	5.35	0.3722	0.4337	0.0452	0.8510
Apple tree	48.04	48.95	3.01	0.4103	0.4171	0.0255	0.8529
Cherry tree	48.99	48.28	2.73	0.4272	0.4198	0.0236	0.8706
Chestnut	49.10	47.09	3.81	0.4552	0.4353	0.0350	0.9255
Feijoa	48.41	49.31	2.28	0.4207	0.4274	0.0194	0.8675
Hazelnut tree	50.16	46.09	3.75	0.4388	0.4021	0.0325	0.8734
Oak tree	45.23	49.51	5.26	0.4180	0.4564	0.0482	0.9225
Orange tree	41.89	52.99	5.12	0.3389	0.4275	0.0411	0.8075
Palm	43.22	52.83	3.95	0.3380	0.4121	0.0306	0.7807
Cardoon	52.02	44.58	3.40	0.4864	0.4158	0.0315	0.9337
Bamboo	45.80	52.74	1.46	0.3508	0.4028	0.0111	0.7647
Longan	43.66	47.03	9.31	0.4263	0.4589	0.0914	0.9766

Biochemical methane potential through chemical oxygen demand

COD is commonly used in the water and wastewater industry to measure the organic strength of liquid effluents. It is a chemical procedure using a strong acid oxidation. The strength of organic conversion of biomass can be expressed in ‘oxygen equivalents’ in which a mg of O_2 is required to oxidize the C to CO_2. However, the COD concept can estimate the methane yield. One mole of methane requires 2 moles of oxygen to oxidize it to CO_2 and water, so each gram of methane corresponds to the removal of 4 grams of COD. Total methane production of different plant leaves were presented in Figure 25 and Table 16.

$$\underset{16}{CH_4 + 2O_2} \longrightarrow \underset{64}{CO_2 + H_2O} \qquad \textbf{Eq. 8}$$

Efficiency of pretreatment on longan leaves for biogas production co-digestion with pig manure

Primary characteristics of raw materials

The characterizations of pig manure and longan leave were shown in Table 17. The total solids (TS) and volatile solids (VS) of longan leaves content were 892,473 mg/kg and 833,384 mg/kg, respectively. The average pH was 4.86 and average COD was 114,000 mg/g. The pig manure was used in co-digestion having a total solids (TS) of 373,378 mg/kg and volatile solids (VS) of 280,034 mg/kg, respectively. The average pH that have been recorded was 6.05 and the average COD was 126,857 mg/L. When the TS of raw material is known, the content of the TS can be controlled at the start of the fermentation.

Table 17 Characteristics of raw materials (Pig manure and Longan leave).

Parameter	Pig manure	Longan leaves
COD (mg/g)	126,857	114,000
TS (mg/kg)	373,378	892,473
VS (mg/kg)	280,034	833,384
pH	6.05	4.86

Interactive effect ratios of longan leaves to pig manure on RSM (Central Composite Design)

Table 18 Result from RSM modeling of longan leaves to pig manure (Longan leaves pretreatment by hot water).

Run	Factor 1 A:Time	Factor 2 B:Ratio	Response Biogas yield
	Day	Longan leaves: Pig manure	ml
1	22.5	5 (5: 5)	245
2	0	5 (5: 5)	0
3	0	10 (10: 0)	0
4	0	0 (0: 10)	0
5	22.5	5 (5: 5)	280
6	0	0 (0: 10)	0
7	0	5 (5: 5)	0
8	45	0 (0: 10)	330
9	22.5	10 (10: 0)	195
10	45	5 (5: 5)	1,410
11	22.5	0 (0: 10)	330
12	22.5	10 (10: 0)	160
13	45	0 (0: 10)	345
14	45	10 (10: 0)	610
15	45	5 (5: 5)	1,036
16	0	0 (0: 10)	0
17	0	10 (10: 0)	0
18	0	5 (5: 5)	0
19	22.5	0 (0: 10)	330
20	22.5	5 (5: 5)	210
21	22.5	10 (10: 0)	175

22	45	10 (10: 0)	545
23	22.5	0 (0: 10)	345
24	45	0 (0: 10)	310
25	45	10 (10: 0)	486
26	45	5 (5: 5)	1,236
27	0	10 (0: 10)	0

Table 19 ANOVA for quadratic model (Longan leaves pretreatment by hot water).

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	3.41E+06	7	4.87E+05	30.71	< 0.0001	significant
A-Time	2.26E+06	1	2.26E+06	142.63	< 0.0001	
B-Ratio	37604.17	1	37604.17	2.37	0.1399	
AB	35861.33	1	35861.33	2.26	0.1489	
A^2	57885.63	1	57885.63	3.65	0.0711	
B^2	4.04E+05	1	4.04E+05	25.53	< 0.0001	
A^2B	71645.44	1	71645.44	4.52	0.0468	
AB^2	6.24E+05	1	6.24E+05	39.36	< 0.0001	
Residual	3.01E+05	19	15842.03			
Lack of Fit	2.19E+05	1	2.19E+05	48.41	< 0.0001	significant
Pure Error	81578	18	4532.11			
Cor Total	3.71E+06	26				

Factor coding is Coded. Sum of squares is Type III – Partial.

The Model F-value of 30.71 implied that the model was significant. There was only 0.01% chance that an F-value could occur due to the noise.

P-values that was less than 0.0500 indicated that the models were significant. In this case A, B^2, A^2B, AB^2 were significant to each other. Values greater than 0.1000 indicated that the model terms were not significant to each other. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

The Lack of Fit with the F-value of 48.41 implied that it was significant. There was only a 0.01% chance that a Lack of Fit F-value could occur due to noise. In this case, the significance of lack of fit is not good-the model should be fit. (Table 19)

Table 20 Fit statistics (Longan leaves pretreatment by hot water).

Std. Dev.	125.87	R^2	0.92
Mean	317.70	Adjusted R^2	0.89
C.V. %	39.62	Predicted R^2	0.85
		Adeq Precision	17.91

The Predicted R^2 of 0.8484 was in reasonable agreement with the Adjusted R^2 of 0.8889; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio that is greater than 4 is desirable. In this paper, the ratio of 17.914 indicated an adequate signal for the model to be used to navigate the design space. (Table 20)

Final equation in terms of Actual factors.

$$\text{Biogas yield} = 45.07 + 10.46(A) - 54.09(\text{Ratio}) + 5.13(AB) - 0.07(A^2) + 5.41(B^2) + 0.05(A^2B) - 0.7(AB^2)$$

When A = Time and B = Ratio

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space. (Figure 26)

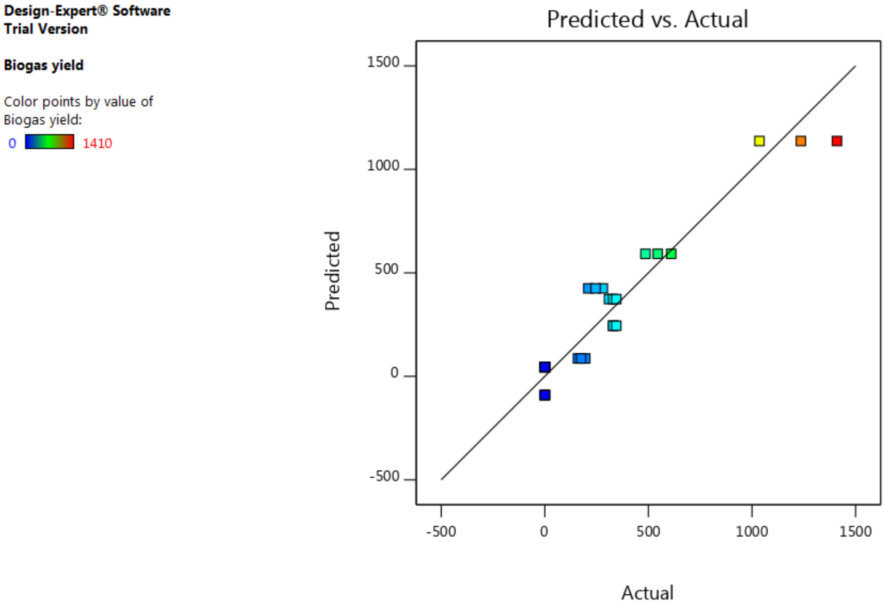

Figure 26 Experimental data plotted against RSM model predicted data of ratio (Longan leaves pretreatment by hot water) for small-flowered nutsedge.

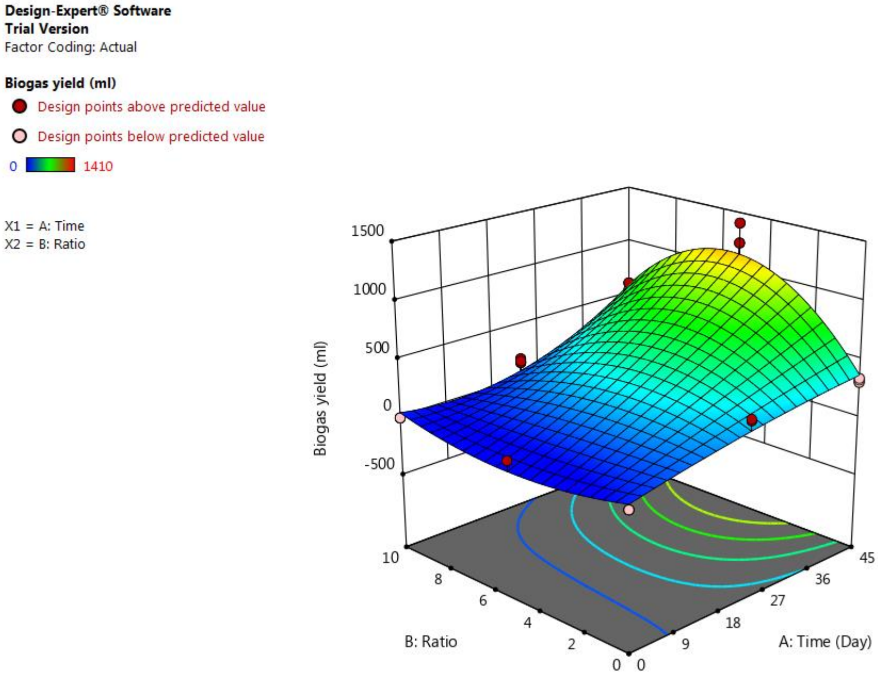

Figure 27 3D plot for longan leaves to pig manure (Longan leaves pretreatment by hot water).

Table 21 Result from RSM modeling of longan leaves to pig manure (Longan leaves pretreatment by NaOH).

Run	Factor 1 A: Time	Factor 2 B:Ratio	Response 1 Biogas yield
	Day	Longan leaves : Pig manure	ml
1	45	10 (10: 0)	925
2	45	0 (0: 10)	310
3	22.5	5 (5: 5)	200
4	22.5	0 (0: 10)	345
5	45	10 (10: 0)	820
6	0	5 (5: 5)	0
7	22.5	5 (5: 5)	275
8	45	10 (10: 0)	825
9	22.5	10 (10: 0)	270
10	0	10 (10: 0)	0
11	22.5	0 (0: 10)	330
12	0	0 (0: 10)	0
13	0	0 (0: 10)	0
14	0	5 (5: 5)	0
15	45	0 (0: 10)	330
16	0	0 (0: 10)	0
17	22.5	5 (5: 5)	400
18	0	10 (10: 0)	0
19	45	5 (5: 5)	1,525
20	45	0 (0: 10)	345
21	0	5 (5: 5)	0
22	45	5 (5: 5)	1,652
23	22.5	10 (10: 0)	310
24	0	10 (10: 0)	0

25	22.5	10 (10: 0)	290
26	22.5	0 (0: 10)	310
27	45	5 (5: 5)	1,502

Table 22 ANOVA for quadratic model (Longan leaves pretreatment by NaOH).

Source	Sum of Squares	df	Mean Square	F-value	P-value	
A-Time	3.65E+06	1	3.65E+06	183.75	< 0.0001	significant
B-Ratio	2204.17	1	2204.17	0.111	0.7427	
AB	2.09E+05	1	2.09E+05	10.54	0.0042	
A^2	1.43E+05	1	1.43E+05	7.18	0.0149	
B^2	6.01E+05	1	6.01E+05	30.28	< 0.0001	
A^2B	91506.25	1	91506.25	4.61	0.0449	
AB^2	9.35E+05	1	9.35E+05	47.11	< 0.0001	
Residual	3.77E+05	19	19857.83			
Lack of Fit	3.35E+05	1	3.35E+05	141.72	< 0.0001	
Pure Error	42519.33	18	2362.19			significant
Cor Total	6.24E+06	26				

Factor coding is Coded. Sum of squares is Type III – Partial.

The Model F-value of 42.20 implied that the model was significant. There was only a 0.01% chance that an F-value could occur due to noise.

P-values that was less than 0.0500 indicated that model terms were significant. In this case A, AB, A^2, B^2, A^2B, AB^2 were significant model terms. Values greater than 0.1000 indicated that the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

The Lack of Fit F-value of 141.72 implied that the Lack of Fit was significant. There was only a 0.01% chance that a Lack of Fit F-value could occur due to noise. In this case, the significance of lack of fit is not good-the model should be fit. (Table 22)

Table 23 Fit statistics (Longan leaves pretreatment by NaOH).

Std. Dev.	140.92	R^2	0.9396
Mean	406.07	Adjusted R^2	0.9173
C.V. %	34.7	Predicted R^2	0.8907
		Adeq Precision	20.3331

The Predicted R^2 of 0.8907 was in reasonable agreement with the Adjusted R^2 of 0.9173; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 20.333 indicated an adequate signal which means the model can be used to navigate the design space. (Table 23)

Final equation in terms of actual factors.

$$\text{Biogas yield} = 55.68 + 7.04A - 66.81B + 7.08AB + 0.01A^2 + 6.68B^2 + 0.06A^2B - 0.86AB^2$$

When A = Time and B = Ratio

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space. (Figure 28)

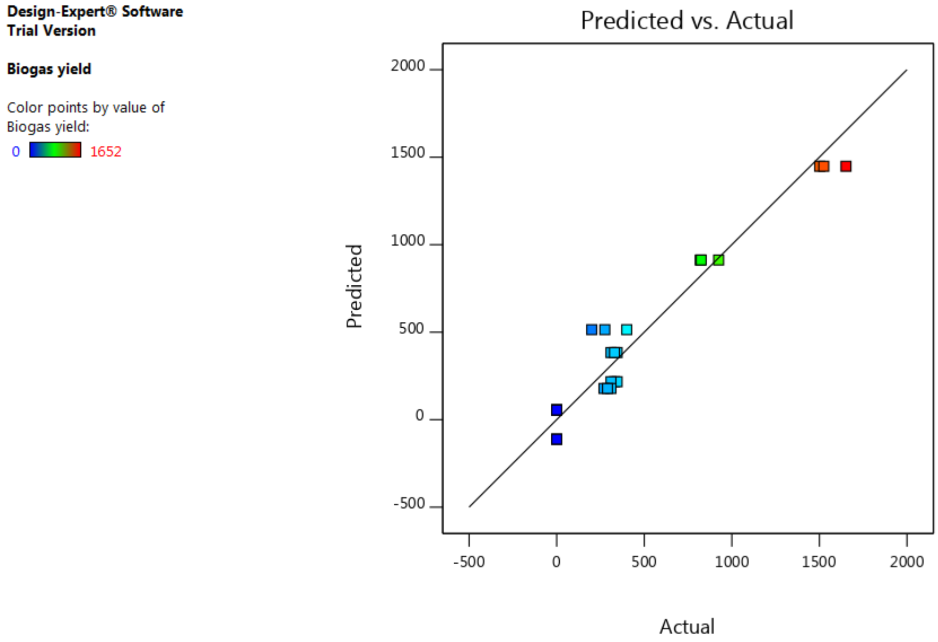

Figure 28. Experimental data plotted against RSM model predicted data of ratio (Longan leaves pretreatment by NaOH) for small-flowered nutsedge.

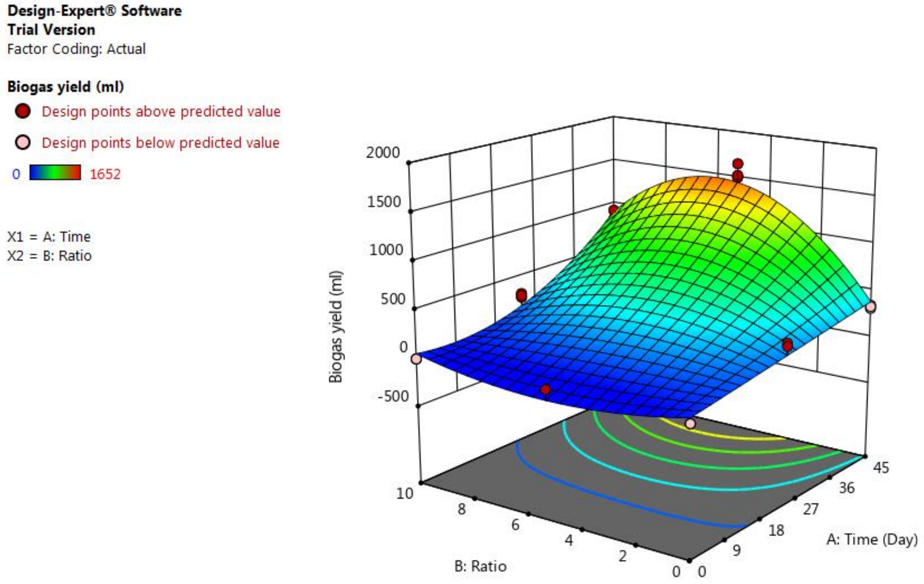

Figure 29 3D plot for longan leaves to pig manure (Longan leaves pretreatment by NaOH).

Table 24 Result from RSM modeling of longan leaves to pig manure (Longan leaves pretreatment by NaOH, 60°C).

Run	Factor 1 A:Time	Factor 2 B:Ratio	Response 1 Biogas yield
	Day	Longan leaves : Pig manure	ml
1	22.5	5 (5: 5)	623
2	22.5	10 (10: 0)	200
3	22.5	5 (5: 5)	525
4	0	5 (5: 5)	0
5	0	5 (5: 5)	0
6	0	5 (5: 5)	0
7	45	10 (10: 0)	890
8	45	10 (10: 0)	1525
9	0	0 (0: 10)	0
10	45	5 (5: 5)	1370
11	22.5	10 (10: 0)	220
12	45	10 (10: 0)	1055
13	45	0 (0: 10)	310
14	0	0 (0: 10)	0
15	22.5	0 (0: 10)	345
16	0	10 (10: 0)	0
17	22.5	5 (5: 5)	720
18	0	0 (0: 10)	0
19	22.5	0 (0: 10)	310
20	45	0 (0: 10)	330
21	0	10 (10: 0)	0

22	45	0 (0: 10)	345
23	22.5	0 (0: 10)	330
24	0	10 (10: 0)	0
25	45	5 (5: 5)	1870
26	22.5	10 (10: 0)	240
27	45	5 (5: 5)	1510

Table 25 ANOVA for quadratic model (Longan leaves pretreatment by NaOH, 60°C).

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	7.492E+06	7	1.070E+06	53.78	< 0.0001	significant
A-Time	3.760E+06	1	3.760E+06	188.95	< 0.0001	
B-Ratio	17604.17	1	17604.17	0.8846	0.3588	
AB	5.146E+05	1	5.146E+05	25.86	< 0.0001	
A^2	87926.69	1	87926.69	4.42	0.0491	
B^2	9.430E+05	1	9.430E+05	47.38	< 0.0001	
A^2B	2.730E+05	1	2.730E+05	13.72	0.0015	
AB^2	7.070E+05	1	7.070E+05	35.53	< 0.0001	
Residual	3.781E+05	19	19901.33			
Lack of Fit	6896.01	1	6896.01	0.3344	0.5703	not significant
Pure Error	3.712E+05	18	20623.85			
Cor Total	7.870E+06	26				

Factor coding is Coded. Sum of squares is Type III – Partial.

The Model F-value of 53.78 implied the model was significant. There was only a 0.01% chance that an F-value could occur due to noise.

P-values that was less than 0.0500 indicated that the model terms were significant. In this case A, AB, A^2, B^2, A^2B, AB^2 were significant model terms. Values greater than 0.1000 indicated that the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

The Lack of Fit F-value of 0.33 implied the Lack of Fit was not significant relative to the pure error. There was a 57.03% chance that a Lack of Fit F-value could occur due to noise. Non-significant lack of fit is good because the model could be fit. (Table 25)

Table 26 Fit statistics (Longan leaves pretreatment by NaOH, 60°C).

Std. Dev.	141.07	R^2	0.95
Mean	471.04	Adjusted R^2	0.93
C.V. %	29.95	Predicted R^2	0.90
		Adeq Precision	20.62

The Predicted R^2 of 0.8900 was in reasonable agreement with the Adjusted R^2 of 0.9343; i.e. the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 20.619 indicated an adequate signal that made the model be used to navigate the design space. (Table 26)

Final equation in terms of actual factors.

Biogas yield = $7.99 + 19.76(A) - 9.59(B) + 4.67(AB) - 0.28(B^2) + 0.96(B^2) + 0.10(A^2B) - 0.75(AB^2)$

When A = Time and B = Ratio

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients were scaled to accommodate the units of each factor and the intercept was not at the center of the design space. (Figure 30)

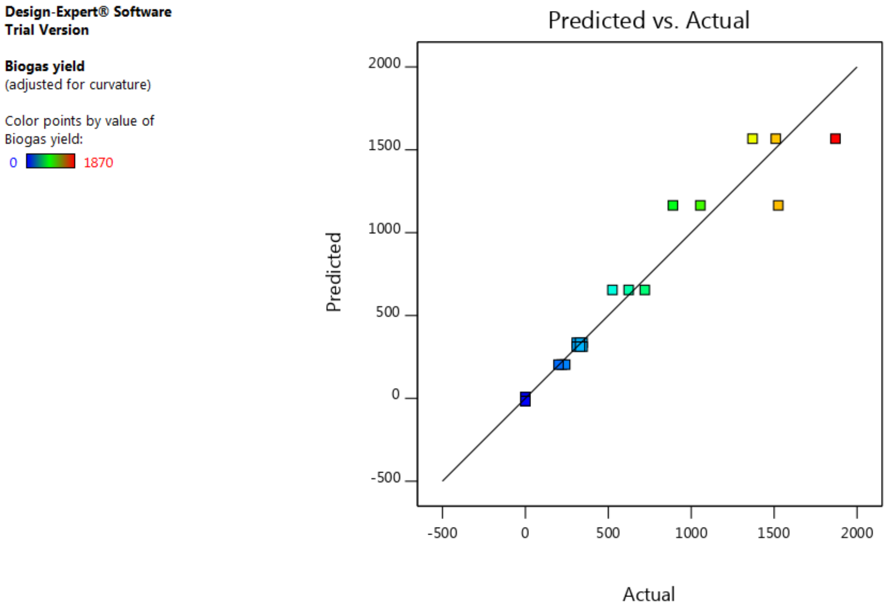

Figure 30 Experimental data plotted against RSM model predicted data of ratio (Longan leaves pretreatment by NaOH, 60°C) for small-flowered nutsedge.

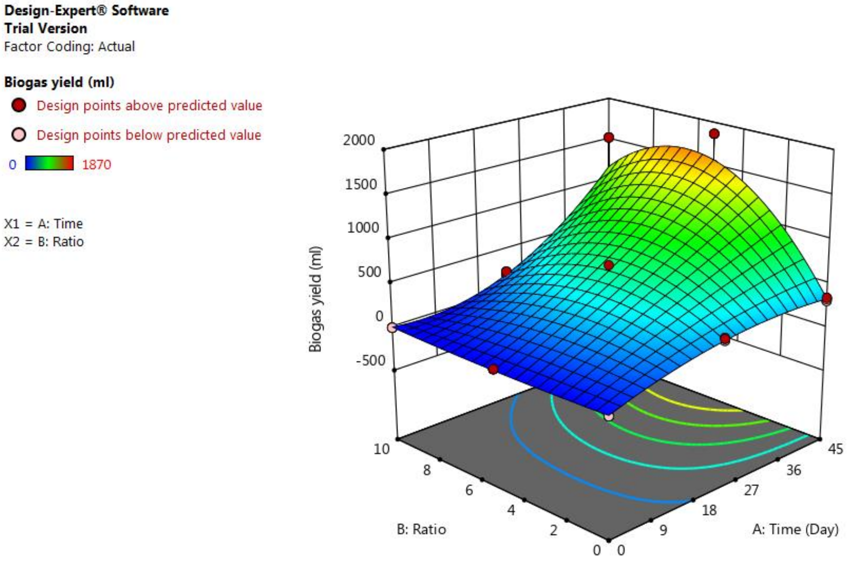

Figure 31 3D plot for longan leaves to pig manure (Longan leaves pretreatment by NaOH, 60°C).

To compare the effect of single substrate digestion and co-digestion with pig manure and longan leaves, the total biogas yield of each combination was shown in Figure 27, 29 and 31. The total biogas productions of most co-digestion systems were higher than the single digestion of either pig manure or longan leaves. Co-digestion uses two or more substrates in which the animal manure contains a lot of useful bacteria for biogas production. Moreover, organic matter such as agriculture wastes provide nutrients for those bacteria. Thus, the co-digestion often increase biogas yield. The anaerobic co-digestion of longan leaves and pig manure were efficient and produced more cumulative biogas. The best ratios were longan leaves: pig manure (5:5) of three pretreatments (Table 18 21 and 24).

Effect of pretreatment on longan leaves by scanning electron microscopy (SEM)

The effect of the 3 pretreatments used in this study were analyzed with the use of SEM. Hot water pretreatment is a physical pretreatment by thermal heat treatment for modification of raw materials to destruction the cellulose tissue. The most often used temperatures are at 100-200°C. However, the material has to be smaller before entering into the process of thermal heat treatment. Stated was the performance of giant reed by hot water pretreatment at 170°C 5 min can extract cellulose and lignin content with 40.20, 4.4% respectively (Jiang et al., 2017).

NaOH pretreatment is a chemical pretreatment by alkali treatment. The methods of pretreatment by alkali treatment can improve the quality of general plant fiber to the effect on lignocellulosic materials. The effect of alkali is based on the amount of lignin contained in fiber (McMillan, 1994). The principles of alkali pretreatment were used to increase swelling within the molecule of hemicellulose and to increase the surface area for bacterial enzyme and to break down the linkage between polysaccharides and lignin. The most common alkalis during alkali pretreatment were sodium hydroxide and ammonium hydroxide. Fu et al. (2018) stated that the performance of *Miscanthus floridulus* pretreatment by 6% NaOH solution was used and the liquid to solid ratio was 10 ml/g and performed at 35°C for

3 h can extract the hemicellulose, cellulose and lignin content with 21.60, 31.63 and 23.98% respectively.

NaOH which increases the temperature pretreatment are physico-chemical methods. This study also used chemical pretreatment to increase the catalyst by increasing the temperature which can lead to the increase of reaction rates. The effect of pretreatment on longan leaves was shown by the SEM images of upper epidermis and lower epidermis of longan leaves before and after pretreatment in Figure 32. Before pretreatment, longan leaf has an intact surface. After pretreatment intact surface of longan leaves had been destroyed. These three pretreatment used in lower leaf epidermis revealed that there were missing plant fibers which might cause the removal of lignin during the process of these pretreatments. The destroyed intact surface could greatly enhance the enzyme access. Therefore, the anaerobic digestion of pretreated longan leaves was more efficient, which can also lead to higher biogas and methane yield from longan leaves (Hendriks and Zeeman, 2009).

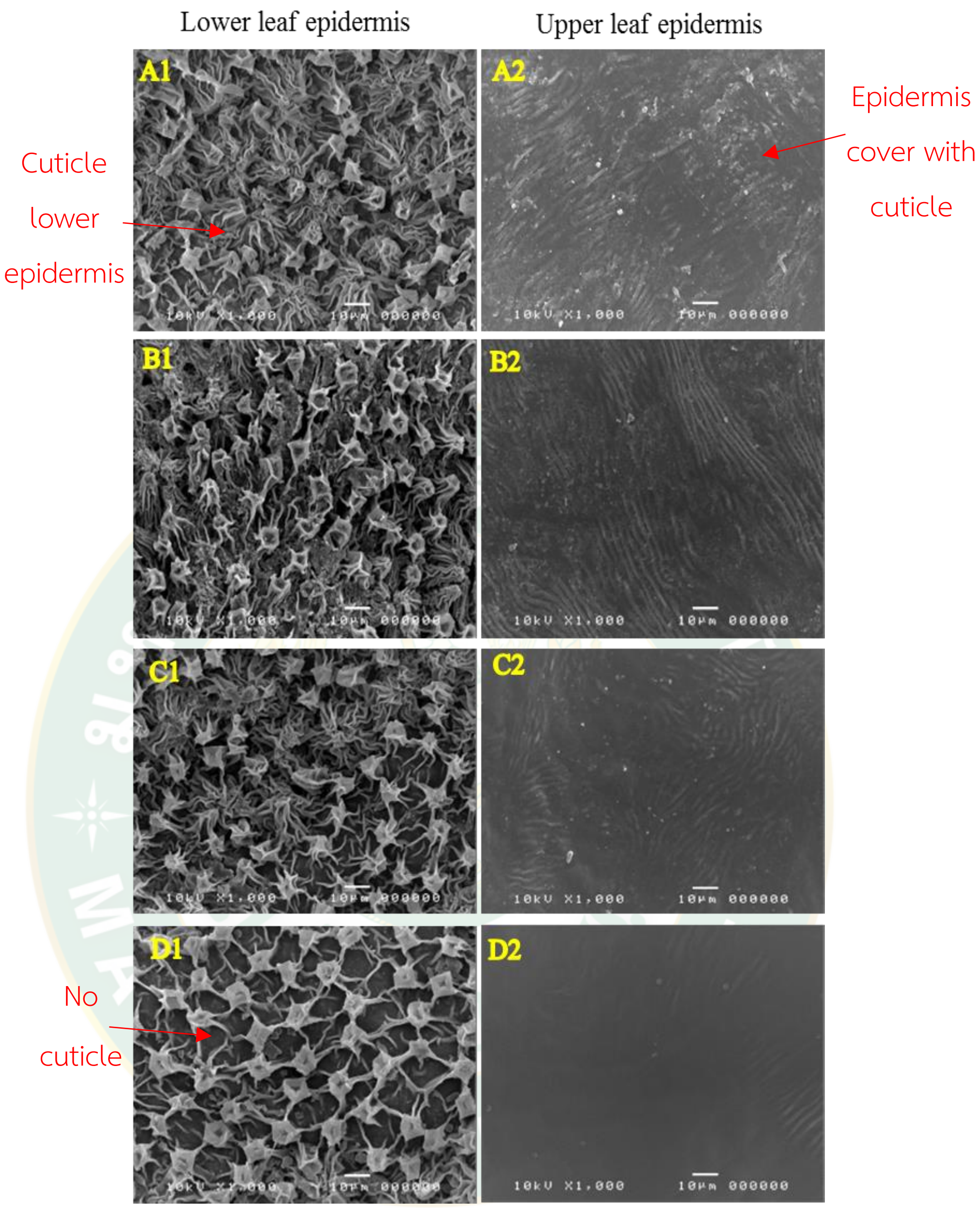

Figure 32 SEM images of untreated and pretreated longan leaves at 1,000X. A) Control B) Hot water pretreatment C) NaOH pretreatment and D) NaOH, 60°C.

Anaerobic digestion process of TS, VS, SCOD alkalinity, pH and VFA in the fermenter.

Table 27 Parameter before and after of anaerobic digestion process.

Parameters	Pretreatment method					
	Hot water		NaOH		NaOH, 60°C	
	Start	End	Start	End	Start	End
TS (mg/L)	93,134^a	71,505^a	97,775^b	63,489^a	96,221^b	64,451^b
VS (mg/L)	66,823^a	47,057^a	67,427^a	38,742^a	66,492^a	39,019^b
SCOD (ml/L)	5,000^a	3,733^a	15,600^b	9600^b	18,666^b	9866^b
Alk (ml/L-$CaCO_3$)	3,705^a	2,070^a	1,517^a	3,617^b	1,150^b	4,183^c
VFA	1,131^a	2,956^a	2,201^b	1,810^a	2,497^c	1,730^b
pH	7.4^a	6.69^a	7.33^a	7.83^b	7.38^a	8.03^b

The ANOVA test was conducted to determine the differences between each cultivar. Values with the same letters indicate no significant difference at P<0.01.

Table 28 Degradation efficiency.

Treatments	Degradation efficiency (%)		Total biogas	CH_4
	TS	VS	productions (ml)	(%)
Hot water	23.22^a	29.59^a	8,903^a	54.5^a
NaOH	33.02^b	41.32^b	12,616^b	60.1^a
NaOH, 60°C	35.07^b	42.54^b	13,221^c	60.7^a

The ANOVA test was conducted to determine the differences between each cultivar. Values with the same letters indicate no significant difference at P<0.01.

The results of total solids (TS) and volatile solids (VS) before and after of an anaerobic digestion process represents the degradability efficiency of organic matter in fermenter. The highest percentage content of TS and VS in the treatment of longan leaves by co-digestion with pig manure pretreatment were derived from 2%NaOH at 60°C with 35.07% and 42.54%, respectively (Table 28). The results showed higher percentage content of TS than that of the obtained 8% best content of biogas production in TS by Song et al. (2012). One of the objective of the SCOD is to measure the organic soluble in liquid. It is a chemical procedure using strong acid oxidation. The parameter of SCOD represents the solution extent of a substrate, which is the equilibrium between the solution of a substrate into SCOD and the consumption of SCOD to produce methane and carbon dioxide. In the beginning of anaerobic digestion, the SCOD concentration of the anaerobic digestion system increased quite quickly. It will decrease gradually, until the end of anaerobic digestion (Fu et al., 2018). The parameter of TS, VS and SCOD were shown in Table 27.

The best pH values of biogas production ranged from 6.8 to 7.2. The process is severely inhibited if the pH value decreases below 6.0 and rises above 8.5 may lead to the inhibition of an anaerobic digestion system (Yuan et al., 2011). The pH values of three treatments were always among 7.3-7.4 similarly. Alkalinity is a determination of alkalinity in the system. The higher the alkalinity, the higher pH and the more possible to achieve stable system which demonstrates the degradation of VFA to produce methane (Zhang et al., 2013). The parameter of Alkalinity, pH and VFA were shown in Table 27.

Efficiency of biogas production

The performance of an anaerobic digestion was showed by the amount of biogas production. Biogas production can be indicated by a digestion rates in co-digestion system other than COD removal efficiency (Suebsagoon Y, 2010). Different pretreatment methods were used in the production of biogas from co-digestion of pig manure and longan leaves. Initial biogas production from all pretreatment method were increased and were decreased after 7 days until there was no methane production was observed. During the early stage of anaerobic digestion, the non-methanogen bacteria produce volatile fatty acid from macromolecule and methanogens which were adapted to the acidic environment that causes the initial increase of biogas production (Wang et al., 2017). The maximum peaks of biogas production of 2%NaOH at 60°C pretreatment,

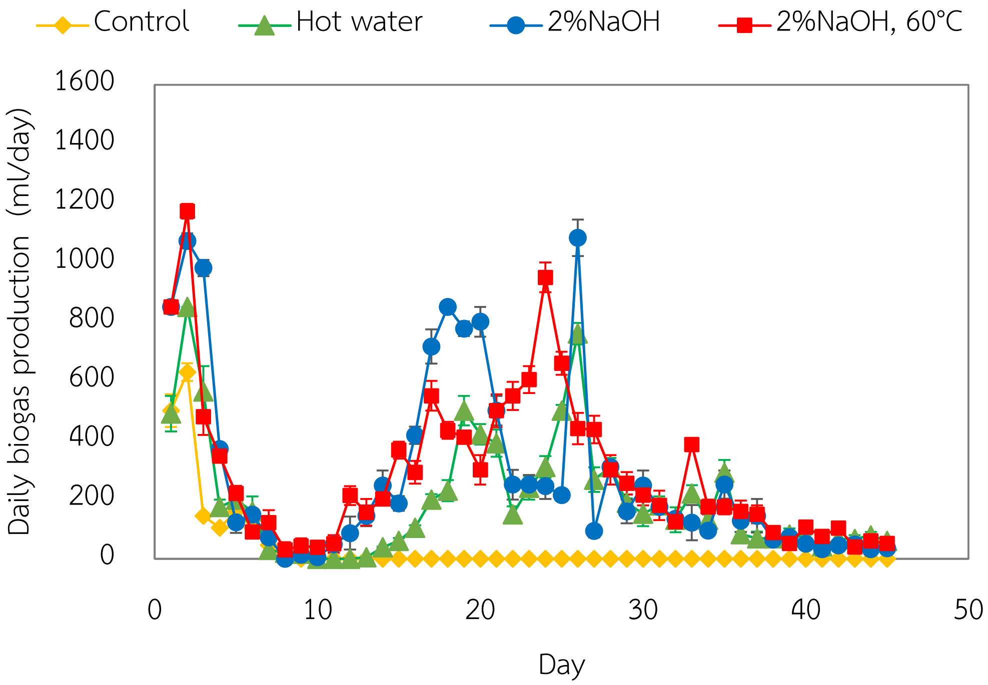

Figure 33 Daily biogas production from co-digestion process by difference of longan leaves pretreatment method.

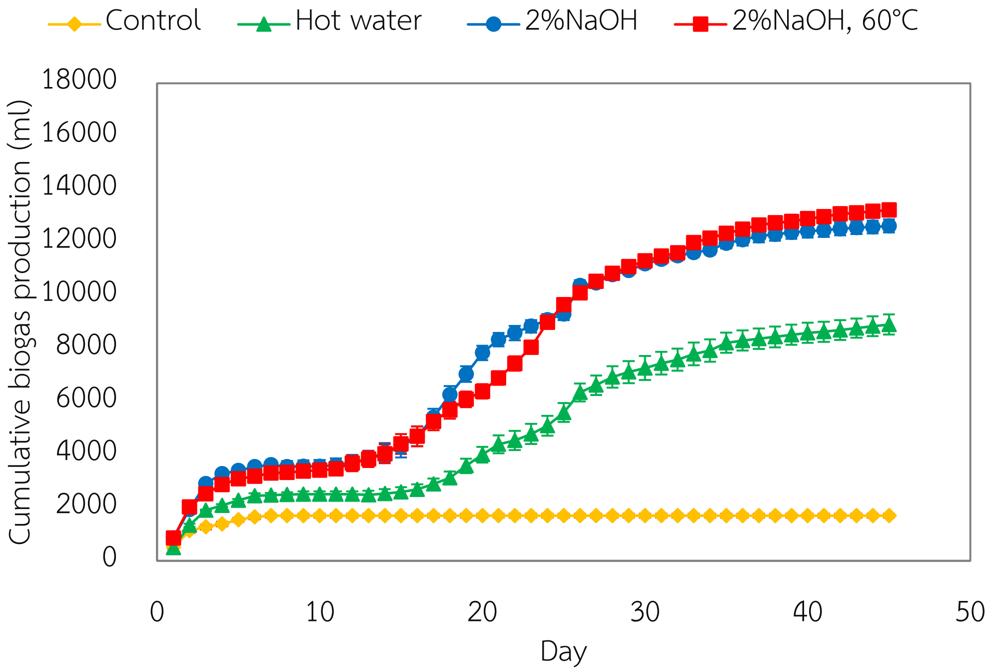

Figure 34 Cumulative biogas production from co-digestion process by difference of longan leaves pretreatment method.

2%NaOH pretreatment and Hot water pretreatment were 950 ml, 1083 ml and 760 ml, respectively. However, in the last phase (30-40th days), production of biogas was decreased quickly and became stable as shown in Figure 30 and 31. The cumulative biogas production yield by 2%NaOH at 60℃ pretreatment, NaOH pretreatment and Hot water pretreatment were 13,221 ml, 12,616 ml and 8,903 ml, respectively (Figure 34).

Methane content production from co-digestion process by difference of longan leaves pretreatment method

The percent contents of methane production from co-digestion process by difference of pretreatment method was done. The methanogenic phase is the formation of methane by methanogens bacteria. The biological process here is the breakdown of acetic acid, though other forms of the reaction can also produce methane by direct anaerobic digestion (Rea, 2014). The range of methane content for hot water pretreatment was found to vary from 5.15% to 54.5 %, over a 5 to 45 day period. The maximum methane content observed was 54.5% on the 35th day of fermentation. Methane content of NaOH pretreatment longan leaf substrate range from 5.55 to 60.1% and the maximum methane content was observed on the 30th day of fermentation. Thus, the highest methane content among the three pretreatment used was observed in NaOH at 60℃ pretreatment with a methane content of 60.7% on the 30th day. The results of methane content were shown in Figure 35, 36 and 37. It can be seen that as the methanogenic phase advances, the percent methane contents increases, and the percent carbon dioxide contents decrease, basically in the same proportion (Barlaz et al., 1989). Panyaping et al. (2017) stated that the performance of anaerobic digestion of untreated longan leaves substrate has the highest methane content at 34% on the 15th day of fermentation.

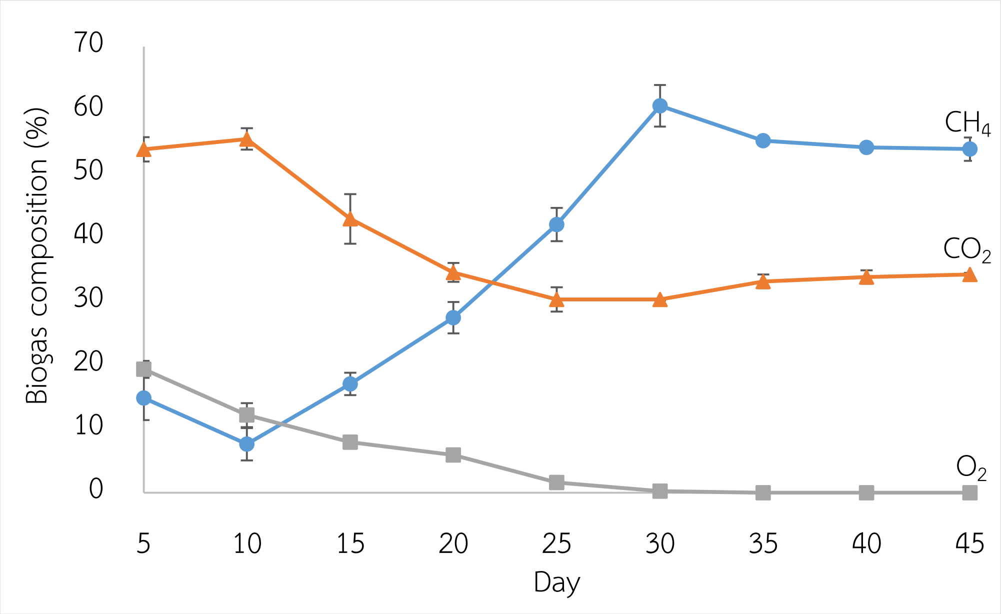

Figure 35 Biogas composition form co-digestion process by 2%NaOH, 60°C pretreatment.

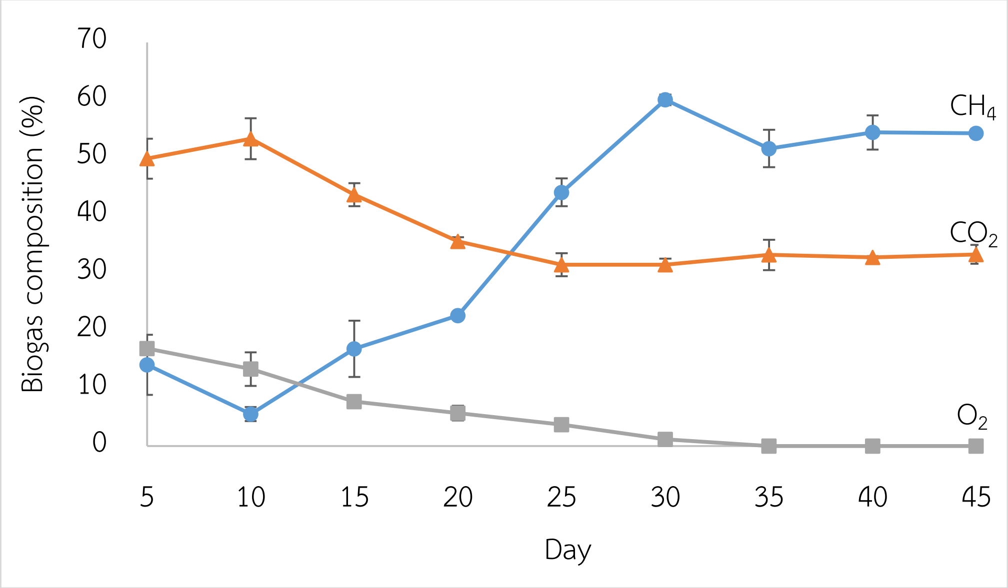

Figure 36 Biogas composition form co-digestion process by 2%NaOH pretreatment.

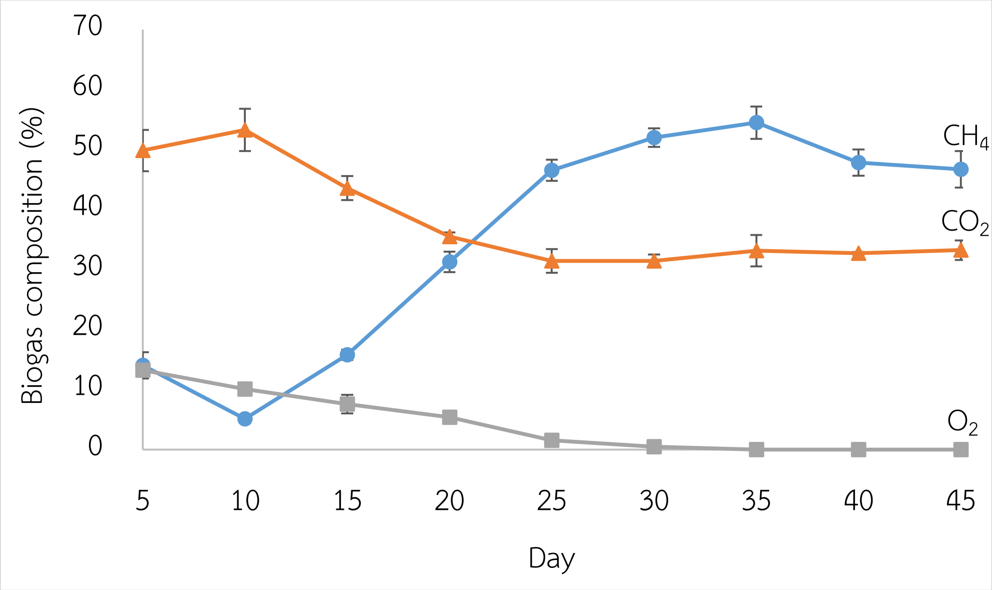

Figure 37 Biogas composition form co-digestion process by Hot water pretreatment.

Enhanced biogas production efficiency of longan leaves co-digestion with pig manure by solar energy

Temperature is an important factor in biogas fermentation. A temperature of 35±2°C has proven as the most efficient for production of biogas, thus it is necessary to use solar heating system to enhanced biogas production efficiency. This study focused in the use of heat from solar energy to increase the temperature of substrate in fermenter to process biogas production more efficiently.

The temperature of the digested slurry inside the biogas digester at control temperature by solar collector

Temperature of digested slurry inside the biogas digester system enhanced biogas production efficiency of longan leaves co-digestion with pig manure by solar energy as shown in Figure 38. The increase of substrate temperature in the biogas digester to control appropriate temperature by solar energy was shown in Figure 23. The appropriate temperature range of substrate should be within 35±2°C which is represented by the red area. Using the solar collector heating, the temperature of the substrate was found to increase to appropriate range. At 1:00 pm to 3:00 am, where the Solar collector heating maintained the temperature, is the periods of time where hot water from the solar collector heating can be used to increase the temperature of the biogas digester. During 4:00 am to 11:00 am, the temperature was observed to decrease continuously. However, after 1:00 pm, the temperature went up in the range of 33-38°C, which was the appropriate temperature for the biogas digester. Thus, according to the result, a solar energy can improve the efficiency of biogas production to increase the temperature of the substrate in biogas digester for 13 h.

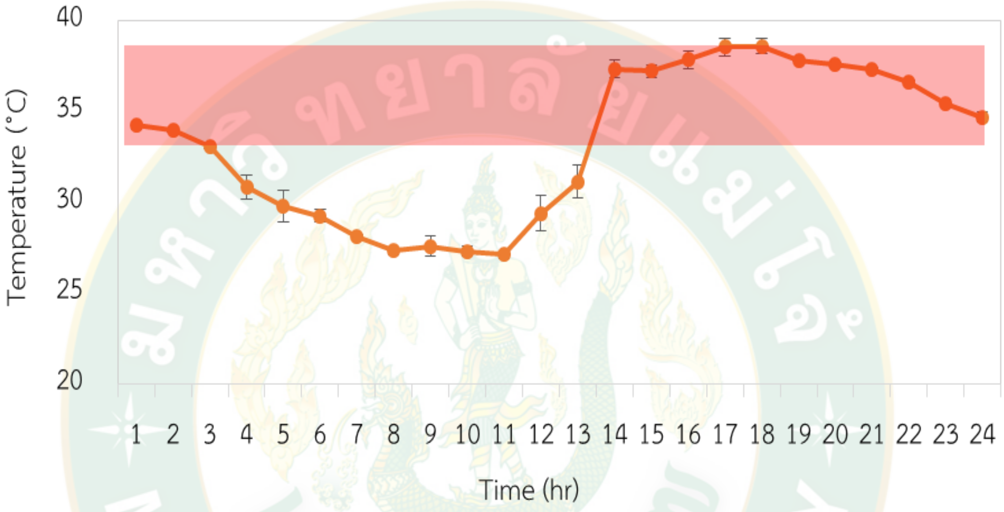

Figure 38 Temperature of the digested slurry inside the biogas digester. (January 2018)

Quantities daily biogas production and methane production of efficiency of longan leaves co-digestion with pig manure by solar energy

Daily total biogas production of longan leaves co-digestion with pig manure in the enhanced fermenter efficiency by solar energy was shown in Figure 39. Biomass for produced energy can be digested either alone or in co-digestion with other materials. After 35 days, the rate of biogas production of longan leaves co-digestion with pig manure gradually declined. The biogas accumulated throughout the research period was 103.2 L/kg from the fresh material and the average total amount of gas was 74 L/day. The maximum peak of biogas in the system was 234 L on the 12th day of the experiment.

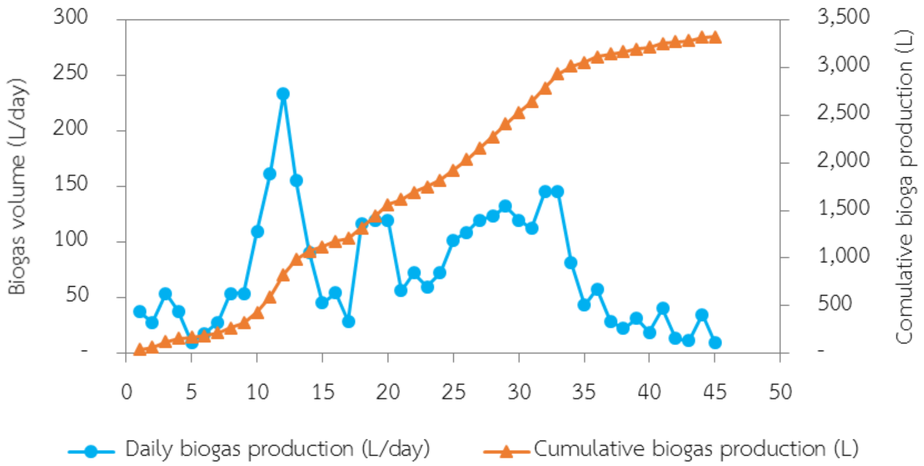

Figure 39 Daily biogas production and cumulative biogas production of co-digestion of longan leaves with pig manure by solar energy.

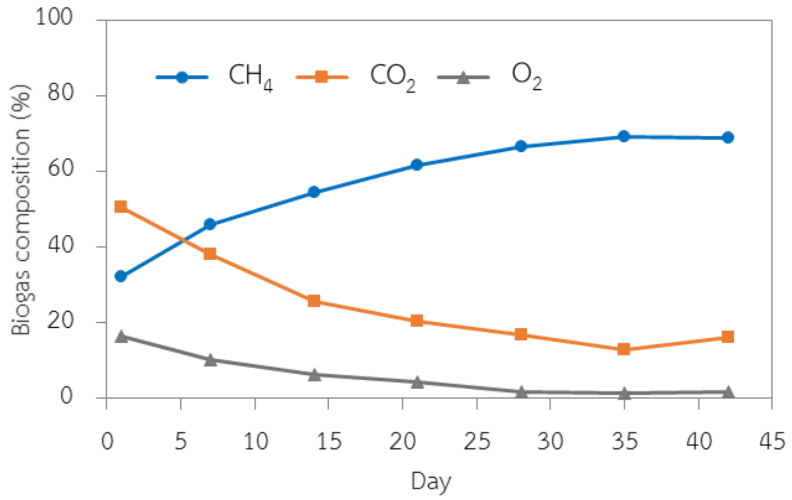

Figure 40 Biogas compositions from enhanced biogas production efficiency of co-digestion of longan leaves with pig manure by solar energy.

Biogas composition results are presented in Figure 40. Biogas composition from experimental measurements starting from methane content of 32.2 on the 1st day. The range of methane content of this system was found to vary from 32.2 to 68.1 % from the 1st to 45th day period. The maximum methane content observed was 68.1% on the 35th day of fermentation. The results showed the percent methane content was increased. On the other hand, the percent carbon dioxide content was found to decrease, basically in the same proportion of the small scale experiment. (Panyaping et al. 2017) stated that the performance of the biogas production of anaerobic digestion of longan leaves substrate had a value of 39 L/day and 34% methane content on the 15th day of fermentation with the rate digester of 200 L at room temperature. The results of this study demonstrated that the biogas yield from the enhanced biogas production efficiency of longan leaves co-digestion with pig manure by solar energy had higher biogas production at room temperature.

Anaerobic digestion process of TS, VS, pH, VFA, SCOD and alkalinity in the fermenter

The experiments were carried out 45 days retention time operated by biogas production of longan leaves with co-digestion with pig manure using heat from solar energy. In this research, the increase of temperature of digested slurry inside the biogas digester showed the temporal variation of TS, VS, pH, VFA and alkalinity. The performance of the biogas digester in terms of TS and VS were shown in Figure. 41a. The TS ranged from 102,107-45,959 mg/L and VS ranged from 66,548-34,202 mg/L respectively. The results of degradability efficiency for TS and VS of the system were 55% in TS and 49% in VS. The volumetric biogas production rate during anaerobic digestion often increases with the decrease in TS and VS by the bacteria during fermentation. The results of degradability efficiency demonstrated that TS and VS which was increased its anaerobic digestion was due to the biomass conversion for biogas production and can be calculated by Specific biogas yield. The calculation process was shown in equation 10. Biogas production of longan leaves with co-digestion of pig manure using heat from solar energy to increase temperature were calculated to specific biogas yield of 195.6 L/kg.TS.

$$\text{Specific biogas yield} = \frac{\textbf{Cumulative biogas production (L)}}{\textbf{Volume the total solids (TS) (kg)}} \qquad \text{Eq. 9}$$

Volatile fatty acids (VFA) are intermediate organic acid products, and the total VFA concentration is considered an important indicator of metabolic status in addition to the pH value during anaerobic digestion. Figure 41c showed the VFA condition in the range of 1252-4110 mg/L. VFA content is important to pH of the system. The increase in volatile organic acids causes the pH to decrease, this may be due to the system having too little amount of methanogens bacteria, or the acidogenic bacteria produce VFA too quickly. In the system of the biogas production of longan leaves with co-digestion of pig manure using heat from solar energy was found to increase the temperature to operate in a balance and effective way. By the first stage of fermentation, the VFA value decreases and increased rapidly showing that the acidogenic bacteria produce VFA from macromolecule and methanogens were adapted to the acidic environment. After that, it will decrease while the pH value will increase. it shoit only showed that the methane producing bacteria can work well.

Figure 41b showed that the pH conditions were at the range of 6.55-7.62 with an average value of 7.11. The pH value is also a crucial parameter of anaerobic digestion. The optimal pH range for anaerobic digestion is 6.8-7.2. The accumulation of intermediate acids leads to pH changes during fermentation. The microorganisms in the anaerobic digester are sensitive to the pH and have different pH optima. The methanogens have a pH optima of between 6.5 and 8.0, while the acetogenic work with a pH between 5.0 and 8.5 (Dussadee et al., 2017). The efficiency of the system will decrease too quickly when pH fell below 6.2. It is due to the acetogenic bacteria can degrade the VFA in small amount that causes the VFA accumulation and pH value to decrease. During the biogas production of the system, the increase in pH showed that there is no VFA accumulation.

The parameter of SCOD (Figure 41f) represents the solution extent of a substrate, which is the equilibrium between the solution of a substrate into SCOD and the consumption of SCOD to produce methane and carbon dioxide. In the beginning of anaerobic digestion, the SCOD concentration of the anaerobic digestion system increased quite quickly and decreased gradually, until the end of anaerobic digestion (Fu et al., 2018).

Alkalinity is a determination of alkalinity in the system. The higher the alkalinity, the higher the pH and the more possible it is to achieve stable system which demonstrates the degradation of VFA to produce methane (Zhang et al., 2013). Figures 41d showed the changes of ALK opposite with VFA. The pH parameter dropped quickly for the first 15 days of fermentation. This is the activities of acidogenic bacteria that produce VFA. As the alkalinity also reflected the same trend as pH.

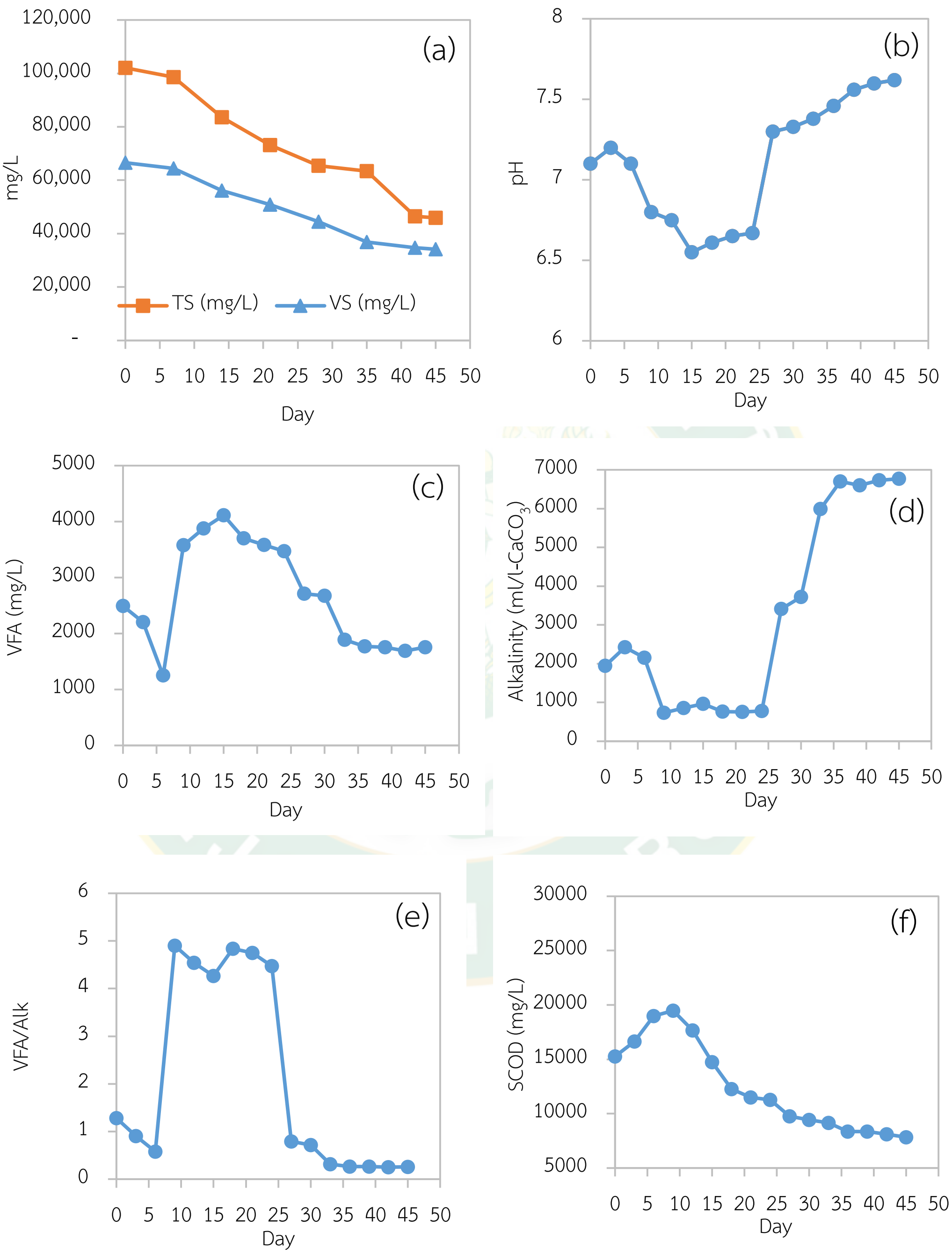

Figure 41 a-f are experiment results of TS, VS, pH, VFA SCOD and alkalinity.

Digestate fertilizer

The composition of digestete from co-digestion of longan leaves with pig manure that show in the Table 29.

Table 29 Chemical compositions of digestate from the co-digestion.

Longan leaves and Pig manure	**Plant nutrition (g/kg in the form of dry matter)**
Nitrogen	84.38
Phosphorus	22.04
Potassium	36.44
Sulfur	6.00
Calcium	45.36
Magnesium	16.07
Ferries	2.73
Manganese	1.0
Sync	0.37
Copper	0.09

Mass balance for biomass and biogas production

Figure 42 presented the mass balance for the scale up of fermentation system. In order to get the mass balance for this system, this experiment has an input of longan leaves of 9.52 kg, pig manure of 22.71 kg and water to adjust the level and mixed all together at the fermenter. The mixture came up with 103.2 L/kg or 195.6 L/kg biogas and the average TS was 74 L/day and the sludge became fertilizer for about 16.44 kg.

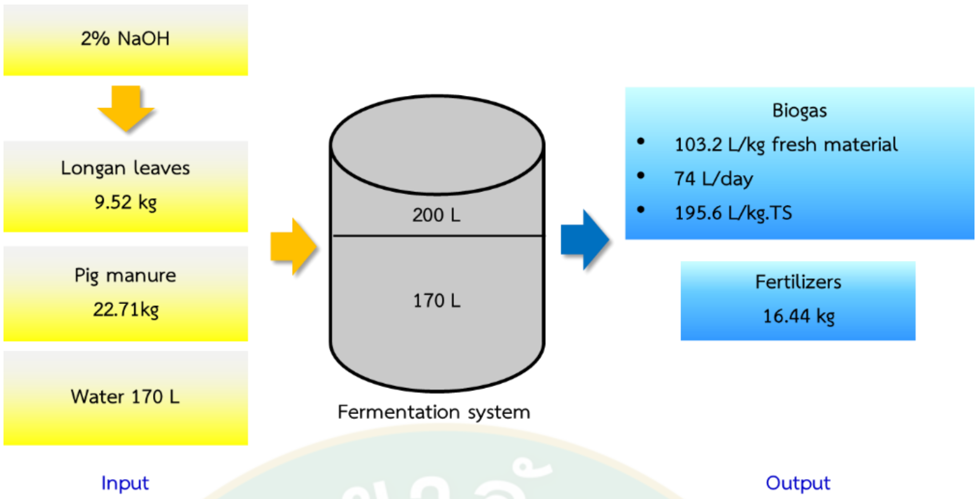

Figure 42 Block diagram for fermentation system.

Biogas purification through chemical process by NaOH

NaOH solution is another alternative absorbent for CO_2 removal. This experiment used NaOH to improve the efficiency of biogas. The absorption of CO_2 into sodium hydroxide solutions has been widely studied. The reaction equations of CO_2 with sodium hydroxide solution can be written as the following scheme:

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+ \qquad 1$$

$$CO_2 + OH^- \rightarrow HCO_3^- \qquad 2$$

$$HCO_3^- + OH^- \rightarrow CO_3^- + H_2O \qquad 3$$

Reaction (1) has a negligible effect on the rate of CO_2 absorption in alkaline solution with PH>10. Reaction (2) is followed by an instantaneous reaction (3). The overall reaction between CO_2 and NaOH solution can be

Expressed as:

$$CO_2 + 2OH^- \rightarrow CO_3^- + H_2O \qquad 4$$

Reaction (4) is second-order and may be considered to be irreversible (Yincheng et al., 2011).

Table 30 showed the CO_2 removal efficiency profile of biogas with CO_2 content of 16.5 % at 12 L under different concentrations of NaOH (1, 2, and 3%) at 5 L for 20 min. The flow rate was set up at 7.6 L/min according to (Yincheng et al. 2011). The percentage of components of the output biogas were tested by gas checker (BIOGAS 5000, Geotech). Based on the results of the three concentrations of NaOH, CO_2 can be removed in all concentrations of NaOH. These results gave higher methane content and all three concentrations of NaOH gave no difference.

Enhanced biogas (from co-digestion of pig manure and longan leaves) HCV was 31.87 MJ/m^3 and the LCV was 28.71 MJ/m^3 which were much higher than biogas production from traditional AD (LCV of 18.0-23.4 MJ/m^3 and HCV of 20.0-25.9 MJ/m^3) (Chuanchai and Ramaraj, 2018). Accordingly, the results of this study verified that high-calorific biogas was obtained in this study system after methane was enriched through biological biogas purification.

Table 30 Test and evaluation of the system performance through chemical upgrading.

Component	Biogas production analysis			
	Before the system improve	After the system improvement		
		1%NaOH	2%NaOH	3%NaOH
CH_4 (%)	68.1	77.7	79.9	77.5
CO_2 (%)	16.5	0.0	0.0	0.0
O_2 (%)	1.8	2.2	2.1	2.1
H_2S (ppm)	89	47	46	50

Economic analysis

In this work, a real experiment (scale 200 L) in biogas production from longan leaves co-digestion with pig manure was used for evaluation. All of the value of currency used in this test is on the year of 2018. Biogas and bioenergy technologies have been proven the environmentally safer with fewer or lowest health impacts, economically effective and helpful in energy conservation. This study was calculated by use of average cost or unit cost which is equal to the total cost divided by the number of goods produced (the output quantity, Q) (Table 31). And the payback period in the system of a scale of 2,000 L for biogas production from co-digestion of longan leaves and pig manure was shown in Table 32.

Table 31 Economic analysis of biogas production from co-digestion of longan leaves and pig manure (the output quantity, Q).

No1.	Item	Economic Analysis	Units
	Electrical		
1.1	-System (0.264 kW/day) 45 day x 4 baht/kW)	26.42	Baht
	-Blender (0.092 kW/time) x 4 baht/kW)	0.15	
	Media and chemicals		
1.2	-NaOH 15 baht/kg (0.6kg/time)	20	Baht
	-Water (0.17 m^3/time) x 9.50 baht/m^3	1.62	Baht
	Total fixed costs	48.19	Baht
2	Quantity (Biogas production)	3.3	m^3
	Average Total Costs=$\frac{\textbf{Total fixed costs}}{\textbf{Quantity}}$	14.03	Baht/m^3

Table 32 Economic analysis of biogas production from co-digestion of longan leaves and pig manure scale 2,000 L (payback period).

No1.	Item	Economic Analysis	Units
1	Initial investment 2,000 L	50,000	Baht
2	Annual expenses		
2.1	Maintenance	2,000	Baht/year
2.2	Electrical		
	- System (0.264 kW/day x 360 day x 4 baht/kW)	380.16	Baht/year
	- Blender (1.08 kW/time x 8 time/year x 4 baht/kW)	34.56	Baht/year
2.3	Media and chemicals		
	- Water 9.50 baht/m^3 (1.7m^3/time) x 8 time/year	129.2	Baht/year
	- NaOH 15 baht/kg (6kg/time) x 8 time/year	720	Baht/year
	Annual expenses	3263.92	Baht/year
3	Profit		
	Biogas production 1 time = 33 m^3 x 8 time/year	264	m^3/year
	- 1 LPG (15 kg) 380.00 Baht	25.33	Baht/kg
	-Biogas 1 m^3 = LPG 1 kg	25.33	Baht/m^3
	- Biogas 264 m^3/year x 25.33 Baht/m^3	6687.12	Baht/year
4	Profit (6687.12 Baht/year - 3263.92 Baht/year)	3423.2	Baht/year
5	Payback period (50,000 Baht/3423.2 Baht/year)	14.61	year

The efficiency of the biogas production of longan leaves co-digestion with pig manure by solar energy was increased when a temperature of the substrate in the biogas digester was at 37°C for 8 h. The cost of electricity compared to heating systems with a heater were shown in Table 33.

Table 33 The electrical power used to heat by solar system and the heater.

Device type	**Solar heating system (Water pump 0.5 HP and motor 0.5 HP)**	**1,000W Heater**
- Time to increase the temperature 37°C	8 h	3.29 h
- Power	0.264 kWh	3.29 kWh
- Energy saving	3.026 kWh	
- Cost saving	12.104 Baht/Day	

Note: 1 kWh = 4 Baht.

Control temperature at 37°C 8 h working time of heater 3.29 h, Calculate the electrical power of the heater at Appendix A

CHAPTER 5

SUMMARY

This study investigated the potential of longan leaves as a feedstock for biogas production. The results indicated that Longan leaves contained rich amount of organic substances and these substances are suitable to use in anaerobic fermentation process to sustain microbial life and transform nutrients into biogas. It was found out that longan leaves and pig manure fermentation can produce as much as 74 L of biogas a day. In the laboratory scale part, 60.7% concentrated CH_4 was generated from the best ratio of 5:5 from RSM analysis with pretreatment process using 2%NaOH and a temperature maintained at 60°C by solar dryer for 72 h. While the scale up part, biogas production by co-digestion longan leaves with pig manure by 2%NaOH for pretreatment yielded a 3,325 L of biogas with a methane concentration of 68.1%. Addtionally, it was observed that the biogas production can be enhanced in a biogas digester when the substrate temperature was increased in 37°C for 8 h. Moreover, CO_2 removal in the biogas was found to be efficient through the use of different concentrations of NaOH (1, 2, and 3%), which resulted to the purification of methane to 78% from 68.10%.

Biogas and bioenergy technologies have been proven the environmentally safer with fewer or lowest health impacts, economically effective and helpful in energy conservation. The results suggested that co-digestion of longan leaves and pig manure was a promising approach for improving biogas production. Furthermore, the digestate has high nutrient concentrations that can potentially use as fertilizer.

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APPENDIX

APPENDIX A

Calculation

Calculation examples theoretical analysis of longan leaves biogas production by percent.

Content $C_aH_bO_cN_d$	Data from simple (100 g D.M.)	Mole of C, H, O and N (Mole/100 g D.M.)	CH_4 (4a+b-2c-3d)/8	CO_2 (4a-b+2c+3d)/8	NH_3 (b)	CH_4+CO_2 +NH_3
a	47.33	47.33/12 =3.94(a)				
b	5.69	5.69/1 =5.69(b)	4(3.94)+5.69-2(2.53)-3(0.41)=1.9	4(3.94)-5.69+2(2.53)+3(0.41)=2.05	0.41	4.35+2.05+0.41= 4.35
c	40.48	40.48/16 =2.53(c)				
d	5.67	5.67/14 =0.41(d)				
% Content	99.17		(1.9/4.35)100=43.66	(2.05/4.35)100=47.03	(0.41/4.35)100=9.31	100

Molecular weight C=12, H=1, O=16 and N=14

Calculation examples theoretical analysis of longan leaves biogas production by cubic meter.

Mole of C, H, O and N (Mole/100 g D.M.)	CH_4 $(4a+b-2c-3d)/8$	CO_2 $(4a-b+2c+3d)/8$	NH_3 (b)
Mole of CH_4, CO_2 and NH_3	1.9(16)=30.4	2.05(44)=90.2	0.41(17)=6.97
Gas produced with 1 Kg of Waste	30.4(1/99.17 (0.717)) $= 0.4263\ m^3$	90.2(1/99.17 (1.977)) $=0.4589\ m^3$	6.97(1/99.17(0.769)) $= 0.0914\ m^3$
Total theoretical amount of gas	$0.4263+0.4589+0.0914=0.9766\ m^3/kg$		

Molecular weight CH_4=16, CO_2=44 and NH_3=17

Mass of the CH_4, CO_2 and NH_3 gas at one atmosphere 0 degrees °C, the density of CH_4, CO_2 and NH_3 gas is 0.717, 1.977 and 0.769 grams per liter. Multiply the volume, in liters, by 1.977 to get the number of grams of CO_2.

Calculation the electrical power of the 1,000W heater control temperature at 37°C 8 h.

-Heater increases the temperature 27 to 37°C, Working time 1.97 h

$$t = \frac{MCP(T_f - T_i)}{\mathbf{Qheater}}$$

$$t = \frac{\mathbf{170(4{,}175)(37-27)}}{\mathbf{1{,}000}}$$

$$t = \frac{\mathbf{70{,}975}}{\mathbf{3{,}600}} = 1.97 \text{ h}$$

-Heater increases the temperature 36 to 37°C, Working time 0.197 h

$$t = \frac{\mathbf{170(4{,}175)(37-36)}}{\mathbf{1{,}000}}$$

$$t = \frac{\mathbf{7.097.5}}{\mathbf{3{,}600}} = 0.197 \text{ h}$$

-1,000W heater control temperature at 37°C 8 h, Working time

$$\text{Working time} = \frac{\mathbf{8}}{\mathbf{1.197}} = 6.68 \text{ time}$$

Working time = 6.68 x 0.197 = 1.32 h

-Total working time of heater = 1.97 + 1.32 = 3.29 h

- Calculation the electrical power of the 1,000W heater control temperature at 37°C 8 h.

$$\text{Electrical power} = \frac{\mathbf{1{,}000}\ x\ \mathbf{3.29}}{\mathbf{1000}} = 3.29 \text{ kWh}$$

Calculation heat exchanger for 200 L biogas digester system

- Desired energy to increases the temperature 26 to 38°C by use time 15 min.

$$Q=MCp\frac{\Delta T}{\Delta t}$$

$$Q= 170\ \text{kg} \times 4.187\ \text{kJ/kg°C} \times \left(\frac{38-26}{900s}\right)\text{°C}$$

$$Q= 9.49\ \text{kW}$$

-Length of heat exchanger has diameter 2 cm (black iron pipe),

ΔT; Difference between outside and inside temperature of black iron pipe when heat transfer = 1°C

$$Q = kA\Delta T$$

$$9490\ \text{W} = (50\ \text{W/m°C})\left(\frac{2\pi L}{In\left(\frac{r2}{r1}\right)}\right)(1\text{°C})$$

$$9490\ \text{W} = (50\ \text{W/m°C})\left(\frac{2(3.14)L}{In\left(\frac{1.05}{1}\right)}\right)(1\text{°C})$$

$$L = 1.452\ \text{m}$$

APPENDIX B

The statistical analysis

Oneway

Notes		
Output Created		01-May-2018 01:07:43
Comments		
Input	Active Dataset	DataSet0
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	Weight	<none>
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Missing Value Handling	Definition of Missing	User-defined missing values are treated as missing.
	Cases Used	Statistics for each analysis are based on cases with no missing data for any variable in the analysis.
Syntax		ONEWAY Totalbiogas BY Treatment /STATISTICS DESCRIPTIVES /MISSING ANALYSIS /POSTHOC=DUNCAN ALPHA (0.05).
Resources	Processor Time	00:00:00.078
	Elapsed Time	00:00:00.110

Descriptives

Total biogas

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
Hot water	3	8.9033E3	382.95996	2.21102E2	7952.0080	9854.6586	8510.00	9275.00
2%NaOH	3	1.2617E4	246.08603	1.42078E2	12005.3551	13227.9782	12335.00	12790.00
2%NaOH, 60°C	3	1.3222E4	257.50405	1.48670E2	12581.9912	13861.3422	12940.00	13445.00
Total	9	1.1581E4	2041.74932	6.80583E2	10011.1281	13149.9830	8510.00	13445.00

ANOVA

Total biogas

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3.280E7	2	1.640E7	179.890	000
Within Groups	547050.000	6	91175.000		
Total	3.335E7	8			

Post hoc tests homogeneous subsets

Total biogas

Duncan

Treatment	N	Subset for alpha = 0.05		
		1	2	3
Hot water	3	8.9033E3		
2%NaOH	3		1.2617E4	
2%NaOH,60°C	3			1.3222E4
Sig.		1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

Oneway

Notes		
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Comments		
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Missing Value Handling	Definition of Missing	User-defined missing values are treated as missing.
	Cases Used	Statistics for each analysis are based on cases with no missing data for any variable in the analysis.
Syntax		ONEWAY Metame BY Treatment /STATISTICS DESCRIPTIVES /MISSING ANALYSIS /POSTHOC=DUNCAN ALPHA (0.05).
Resources	Processor Time	00:00:00.016
	Elapsed Time	00:00:00.109

Descriptives

Methane

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
Hot water	2	60.7000	3.25269	2.30000	31.4757	89.9243	58.40	63.00
2%NaOH	2	60.0500	.91924	.65000	51.7910	68.3090	59.40	60.70
2%NaOH ,60°C	2	3.0450E2	351.99776	2.48900E2	-2858.0744	3467.0744	55.60	553.40
Total	6	1.4175E2	201.68141	82.33609	-69.9017	353.4017	55.60	553.40

ANOVA

Methane

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	79463.110	2	39731.555	.962	.476
Within Groups	123913.845	3	41304.615		
Total	203376.955	5			

Post hoc tests homogeneous subsets

Methane

Duncan

		Subset for alpha = 0.05
Treatment	N	1
2%NAOH	2	60.0500
Hot water	2	60.7000
2%NaOH,60°C	2	304.5000
Sig.		.313

Means for groups in homogeneous subsets are displayed.

Oneway

Notes

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Comments		
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	Filter	<none>
	Weight	<none>
	Split File	<none>
	N of Rows in Working Data File	9
Missing Value Handling	Definition of Missing	User-defined missing values are treated as missing.
	Cases Used	Statistics for each analysis are based on cases with no missing data for any variable in the analysis.
Syntax		ONEWAY TS VS BY Treatment /STATISTICS DESCRIPTIVES /MISSING ANALYSIS /POSTHOC=DUNCAN ALPHA (0.05).
Resources	Processor Time	00:00:00.032
	Elapsed Time	00:00:00.062

Descriptives

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
TS	Hot water	3	22.9933	.61044	.35244	21.4769	24.5097	22.30	23.45
	2%NaOH	3	33.0433	2.49508	1.44054	26.8452	39.2415	30.56	35.55
	2%NaOH,60°C	3	35.0767	3.27985	1.89362	26.9291	43.2243	31.30	37.21
	Total	9	30.3711	5.97761	1.99254	25.7763	34.9659	22.30	37.21
VS	Hot water	3	30.5333	2.83071	1.63431	23.5015	37.5652	27.74	33.40
	2%NaOH	3	41.3233	.71501	.41281	39.5472	43.0995	40.61	42.04
	2%NaOH,60°C	3	42.4933	4.61495	2.66444	31.0292	53.9575	38.78	47.66
	Total	9	38.1167	6.32928	2.10976	33.2516	42.9818	27.74	47.66

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
TS	Between Groups	251.144	2	125.572	21.706	.002
	Within Groups	34.711	6	5.785		
	Total	285.855	8			
VS	Between Groups	260.835	2	130.417	13.120	.006
	Within Groups	59.644	6	9.941		
	Total	320.478	8			

Post hoc tests homogeneous subsets

TS

Duncan

Treatment	N	Subset for alpha = 0.05	
		1	2
Hot water	3	22.9933	
2%NaOH	3		33.0433
2%NaOH,60°C	3		35.0767
Sig.		1.000	.340

Means for groups in homogeneous subsets are displayed.

VS

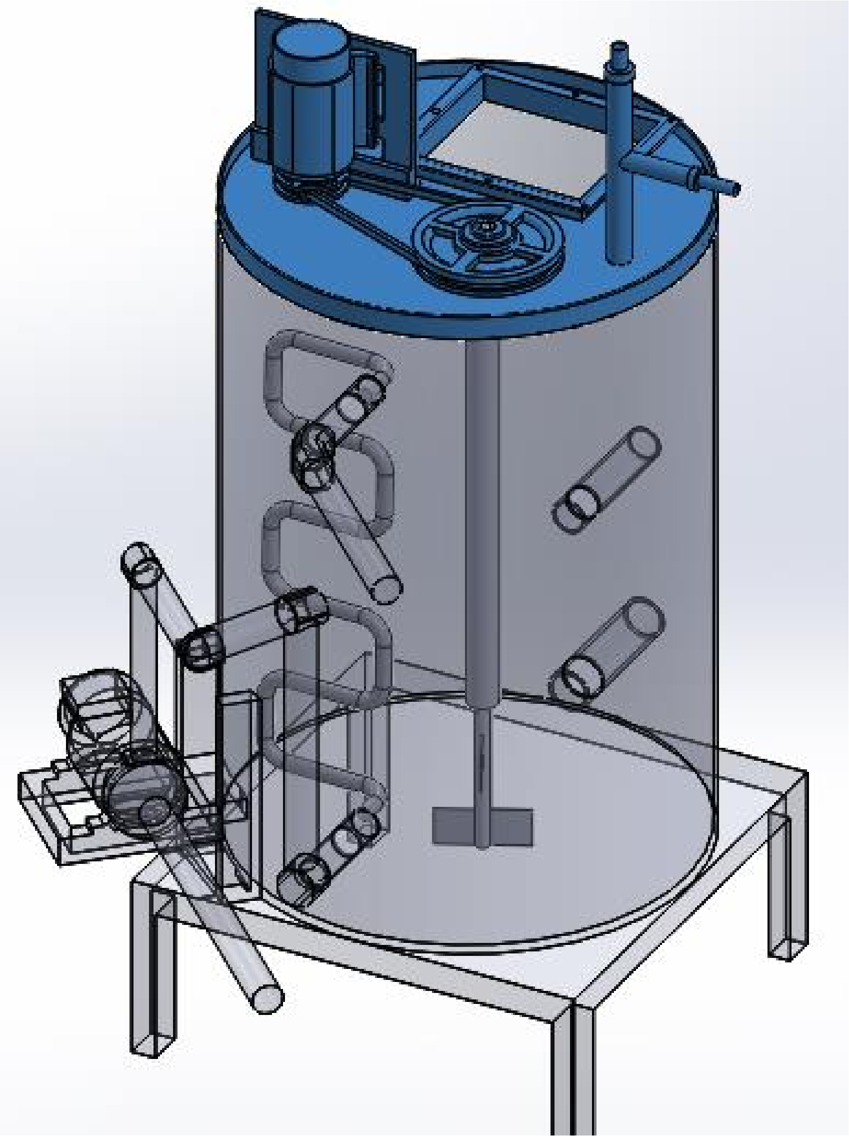
Duncan

Treatment	N	Subset for alpha = 0.05	
		1	2
Hot water	3	30.5333	
2%NaOH	3		41.3233
2%NaOH,60°C	3		42.4933
Sig.		1.000	.665

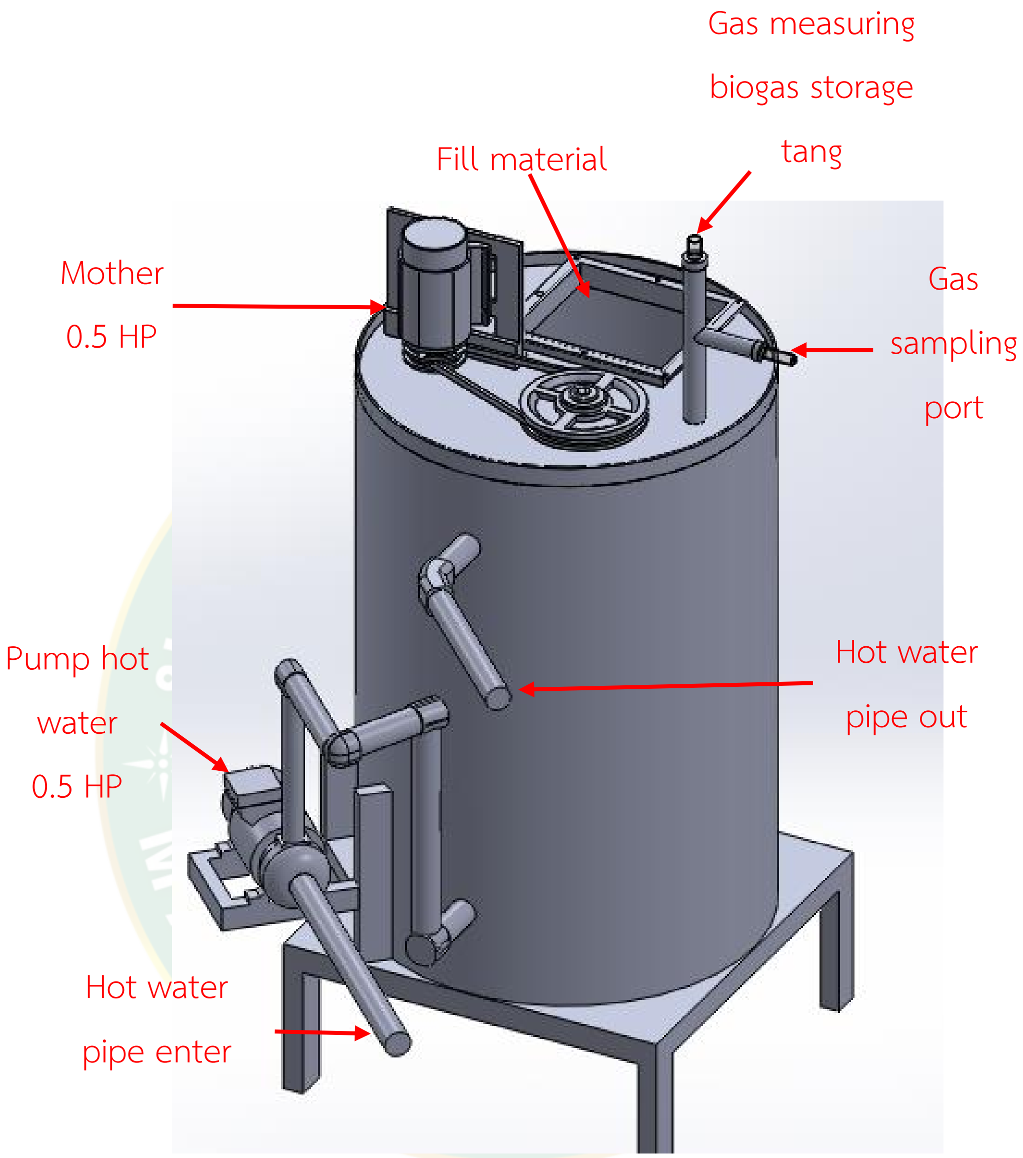
Means for groups in homogeneous subsets are displayed.

APPENDIX C

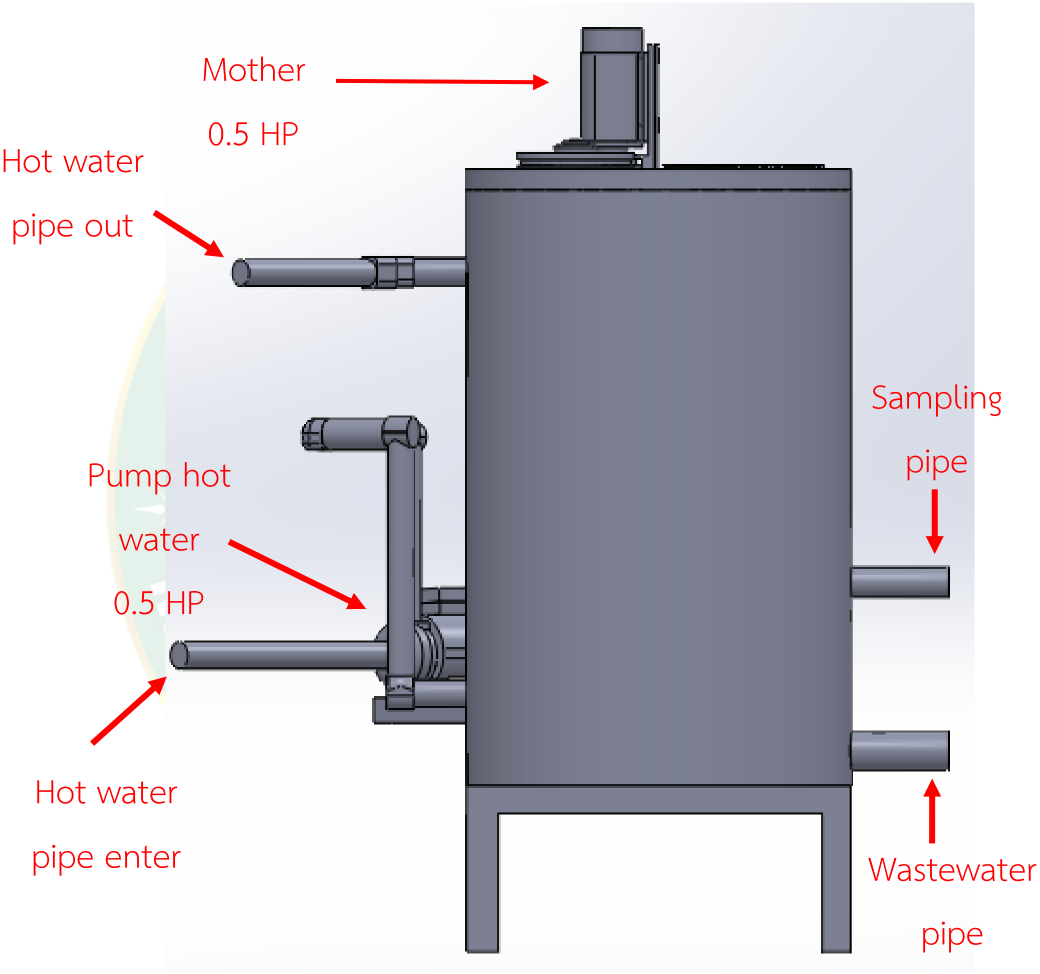
Design of 200 L biogas digester system



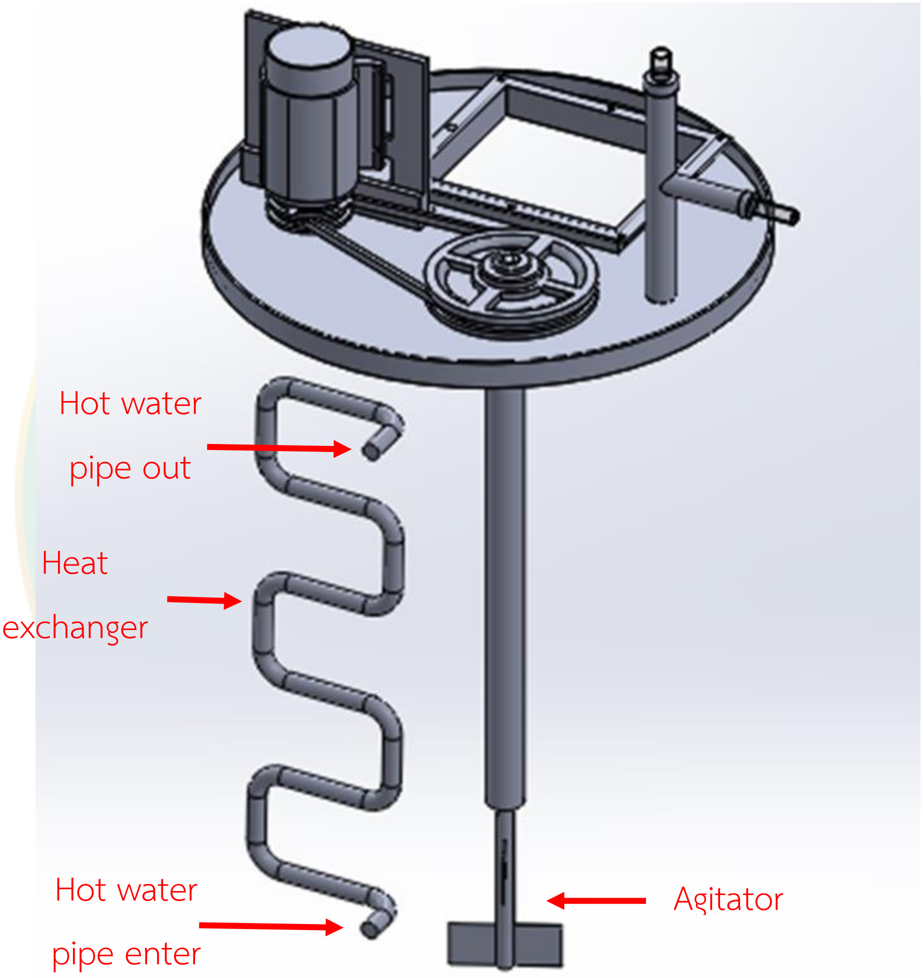
Biogas digester



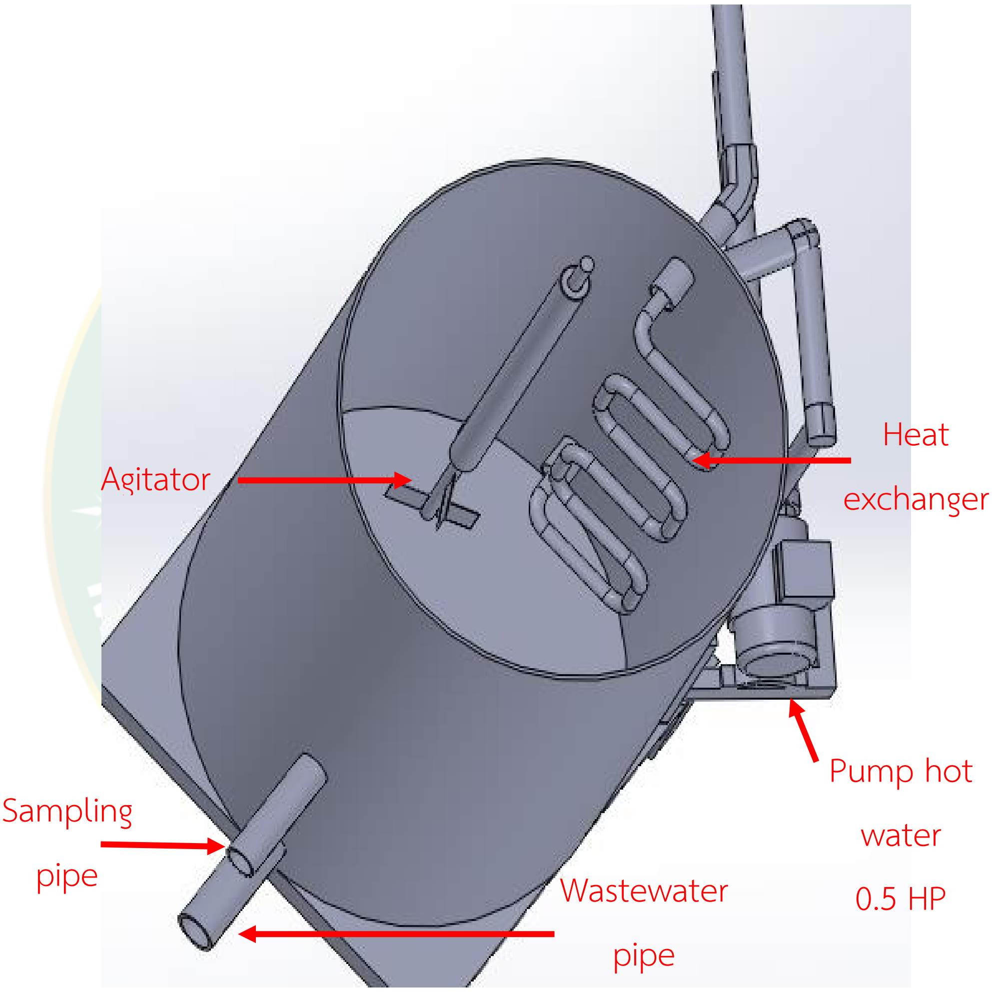
Component external tank



Component external tank



Component internal tank



Component internal and external tank

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